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High energy routes to reactive intermediates: Computational and experimental studies

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HIGH ENERGY ROUTES TO REACTIVE INTERMEDIATES: COMPUTATIONAL AND EXPERIMENTAL STUDIES

BY

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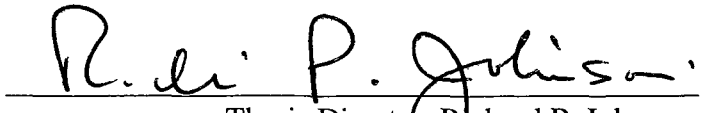

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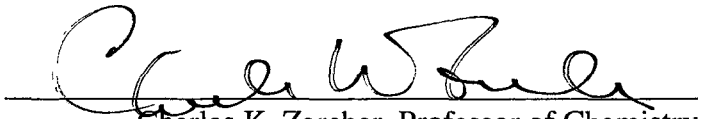

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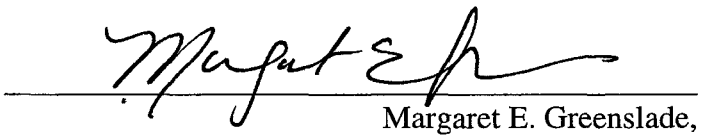

Margaret E. Greenslade,
Assistant Professor of Chemistry

August 2, 2011

Date

DEDICATION

To my parents,

Azra and Muhamed Ajaz

To my brother,

Amir Ajaz

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ABSTRACT

HIGH ENERGY ROUTES TO REACTIVE INTERMEDIATES:

COMPUTATIONAL AND EXPERIMENTAL STUDIES

by

Aida Ajaz

University of New Hampshire, September, 2011

Chapter I

Our continuing efforts to merge the two methods of microwave chemistry and flash vacuum pyrolysis (FVP) are described. We have developed the method of microwave flash pyrolysis (MFP), using graphite and other thermal sensitizers to carry out high temperature reactions previously accomplished by FVP. In a microwave reactor, graphite, carbon nanotubes and other solids heat rapidly to high temperature; various applications of graphite sensitization have been reported. In this thesis, further development and new applications of MFP are described. We have developed a closed vessel MFP method, which utilizes a quartz tube insert for safety. This new method reduces sublimation of substrate from the hot zone, captures all volatile products for analysis and yields a higher conversion to desired products. Studies to date include the following reactions: isomerization of azulene to naphthalene, fragmentation of phthalic anhydride to benzyne, cycloaromatization reactions, and a related collection of

rearrangements. We have extended our earlier studies to new thermal sensitizers including silicon carbide, titanium dioxide and a variety of metal oxides. Graphite remains as the most effective thermal sensitizer.

Chapter II

Thermal interconversion between acetylene and vinylidene, known as the Brown rearrangement, has found importance both synthetically and mechanistically. Generation of a carbene next to C-H bond presented the idea for the synthesis of polycyclic aromatic hydrocarbons. Sealed tube MFP was utilized to investigate the Brown rearrangement of several aryl alkynes. Initial experiments focused on several known structures, specifically 2-ethynylbiphenyl and 2-ethynyltoluene. MFP reaction of 2-ethynylbiphenyl yielded primarily phenanthrene and anthracene with traces of benz[a]azulene. 2-Ethynyltoluene under MFP conditions gave primarily indene and chrysene with additional secondary products. The experimental work was supported by theoretical studies which promoted the investigation of thermal rearrangements and led us to further understanding of the mechanisms. New experiments were designed to explore the limitations of MFP and to understand the mechanistic complexity. Formation of chrysene through an allene intermediate was of interest and it was investigated thoroughly. A synthesis of initial structures that favor [1, 5] hydrogen shift to give an *ortho*-xylallene intermediate was attempted to facilitate formation of higher polyacenes. In addition, novel transformations have been observed for MFP reactions of acetylnaphthalenes.

Chapter III

Computational studies of dehydro-Diels-Alder reaction were performed to help understand the reaction mechanism. CCSD (T)//M05-2X computations have been carried

out for both concerted and stepwise processes in dehydro-Diels-Alder reactions of ethene and ethyne with vinylacetylene and 1,3-butadiyne. All four reactions are exothermic, in spite of high product strain. Concerted transition states for enyne-ene and enyne-yne reactions are ca. 6-7 kcal/mol lower in energy than the stepwise transition states. Diyne-ene and diyne-yne reactions can proceed through a concerted mechanism to give 1,2,3-cyclohexatriene or *ortho*-benzyne, however the computed energy differences between the concerted and the stepwise transition states are <1 kcal/mol.

GENERAL INTRODUCTION

This thesis is divided into three separate chapters: 1) Microwave Flash Pyrolysis; 2) Thermal rearrangements; 3) Computational Studies of Dehydro-Diels-Alder Reaction. Each Chapter is self-contained with its own introduction, results and discussion and conclusion.

CHAPTER I

MICROWAVE FLASH PYROLYSIS

Introduction

Over the past decade, the scope of microwave-assisted organic reactions (MAOS) has broadened rapidly. The use of microwave heating in chemical synthesis was first introduced in 1986 by the research groups of Gedye and Giguere.[1,2] Early microwave experiments were carried out in domestic microwave ovens, but in the past decade specially designed microwave reactors have become common in industrial and research laboratories. Currently, microwave-assisted reactions are well incorporated into areas of organic and medicinal chemistry, as well as in polymer synthesis, material sciences, nanotechnology and biochemical processes. [3] In many reactions, microwave heating reduces reaction time, increases yield, and improves purity of the products.[4,5]

Many substances do not efficiently absorb microwave radiation. This has led to the development of thermal susceptors or sensitizers which absorb the energy and heat reactants. One of the well known sensitizers in microwave chemistry is graphite. The reported number of graphite "sensitized" reactions is limited and some of these reactions may be equally well carried out under ordinary thermal conditions. In the present work, reactions on graphite were investigated because of the potential for high temperature reactions.[6]

Other compounds, such as carbon nanotubes, silicon carbide and selected metal oxides, have been studied and also show promise as efficient thermal sensitizers. Silicon carbide is commonly used as a passive heating element for microwave transparent mixtures.[7] Metal oxides studied to date include WO_3, CuO, SnO and TiO_2. The heating efficiency of such metal oxides in the microwave is proportional to their dielectric loss coefficient.[8]

We have developed the method of microwave flash pyrolysis (MFP), using graphite and other thermal sensitizers to carry out high temperature reactions previously accomplished by flash vapor pyrolysis (FVP). Our work to date includes the following reactions: isomerization of naphthalene to azulene, fragmentation of phthalic anhydride to benzyne, cycloaromatization reactions, conversion of 2-ethynylbiphenyl to phenanthrene, rearrangement of 2-ethynyltoluene to give indene and chrysene, and a related collection of rearrangements.[9]

Microwave Theory

Microwave radiation is electromagnetic energy in the frequency range of 300 to 300,000 MHz. The energy of microwave photons is too low (<0.1 kcal/mol) to break chemical bonds, therefore microwaves directly affect only molecular rotation.[10] Microwave chemistry is based on the efficient heating of materials by microwave dielectric heating effects. Microwave dielectric heating is dependent on the ability of a substance to absorb microwave energy and convert it into heat. A substance must possess a dipole moment to efficiently absorb microwave irradiation. Dipolar polarization and ionic conduction are the two fundamental mechanisms for transferring energy from microwaves to the substance being heated.[4,10]

The heating effect produced by microwaves is dependent on dielectric properties, more specifically dielectric constant and dielectric loss. Dielectric constant measures the ability of the molecules to be polarized by an external electric field. Dielectric loss measures the efficiency with which electromagnetic energy can be converted into heat. The ratio of dielectric loss to dielectric constant is defined as the dielectric loss tangent, tan δ, which is an important number for characteristic microwave heating. A high tan δ is required for efficient microwave absorption and therefore rapid heating.

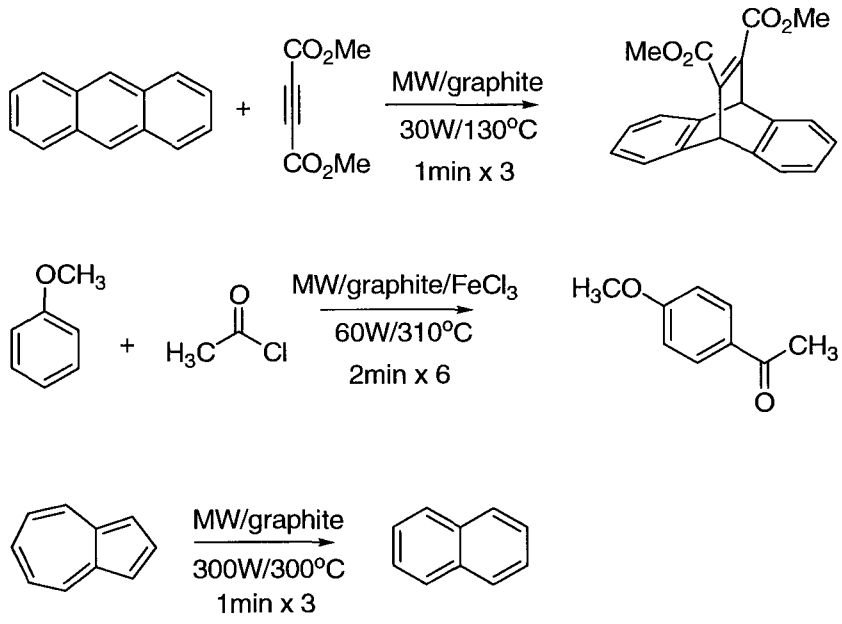
Microwave heating and conventional thermal heating are very different processes. Microwave rradiation couples directly with the molecules present in the mixture, which leads to a rapid increase in temperature throughout irradiated material. In conventional heating, the reaction mixture is in contact with reaction vessel that heats up first and then heat dissipates throughout the reaction mixture. The reaction vessels used in microwave chemistry are made of materials that are transparent to microwave energy.[10]

Graphite- Sensitized Microwave Chemistry

The main focus of this project has been graphite-sensitized microwave chemistry where graphite is used as a "sensitizer". In these reactions, graphite behaves as an energy convertor, conveying energy carried by microwave irradiation to the chemical reagents.[9]

Graphite is the stable form of carbon. The structure of graphite is planar, with each carbon atom in a graphite layer strongly bonded to other three carbons.[11] Weak interlayer bonding is responsible for some of the properties of graphite. Graphite absorbs microwave radiation with high efficiency and also possesses high thermal and electrical conductivity.[11] With high intensity microwave irradiation, this is believed to result in surface temperatures in excess of 1000 °C.[12]

In a microwave reactor, graphite heats rapidly to high temperatures while remaining chemically inert toward many chemical compounds. Applications of graphite as a thermal-sensitizer were initially reported by Laporterie *et al.*[6] and by Besson *et al.*[6,11] Several examples of microwave chemistry, including graphite sensitized microwave flash pyrolysis (MFP) are shown in Scheme 1. Isomerization of azulene to naphthalene by MFP was the first example discovered by Cho in our research group.[13]



Scheme 1: Examples of Graphite-Sensitized Reactions [6]

Exploration of New Thermal Sensitizers

A brief exploration of metal oxides as potential new thermal sensitizers was studied. Metal oxides are stable at high temperature and often have unique catalytic properties.[8] The initial study involved testing the ability of selected metal oxides to absorb microwave irradiation. Metal oxides were subjected to microwave irradiation at 300 °C/150 W for ten minutes (**Table 1**).

Metal Oxide	Maximum Observed Temperature (°C)
TiO_2	>200
Fe_2O_3	137
CuO	300
ZnO	117
Ni_2O_5	155
SnO	301
WO_3	300
CeO_2	134

Table 1: Studied Metal Oxides

Tungsten oxide, copper (II) oxide, and tin oxide absorbed microwave irradiation efficiently and heated to the limiting temperature of 300 °C. These metal oxides show promise as potential thermal sensitizers, however not all the metal oxides reached the set temperature. The rest of the tested metal oxides showed weak to moderate efficiency to absorb microwave irradiation and therefore their use as thermal sensitizers is uncertain.

Results and Discussion

Isomerization of Azulene to Naphthalene

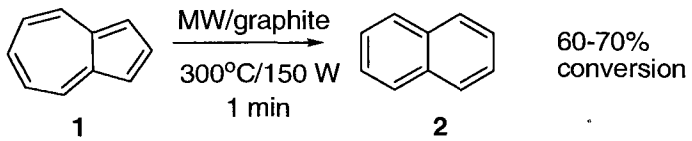
Thermal rearrangement of azulene to naphthalene was first reported by Heibronner in 1947,[14] and later studied by Scott,[15]Alder[16,17] and Wentrup.[18] The mechanism of the reaction that results in a conversion of one aromatic compound to another gained a lot of interest and has been widely investigated.[17] Thermal rearrangement of azulene to naphthalene is usually carried by flash vacuum pyrolysis above 800 °C.

Cho and Johnson studied isomerization of azulene to naphthalene using an MFP open vessel method.[13] In this approach, the substrate and graphite are irradiated under a nitrogen atmosphere for periods of one to five minutes with 100-300 W power at a

limiting temperature of 300 °C. Pyrolysis of azulene under these conditions yielded about 70 % conversion to naphthalene. Carrying pyrolysis at longer times did not result in a higher conversion to product. This is due to a sublimation of reactant and product from the hot zone during the reaction. Cho also studied pyrolysis of azulene with multi-walled carbon nanotubes and amorphous carbon nanopowder. These experiments demonstrated that isomerization is efficiently sensitized with graphite and multi-walled carbon nanotubes but not with amorphous carbon powder.

In the present thesis, we sought development of a closed vessel method. Our goal was to develop a method that will reduce sublimation of a substrate from the hot zone, capture all volatile products for analysis and yield a higher conversion to desired products. Our modification included glassblower-fabricated quartz tubes that fit snugly in a standard CEM Pyrex tube.

Closed vessel experiments are carried out in a quartz tube inserted in a standard Pyrex CEM microwave vial. A glass wool plug was inserted above the graphite layer to minimize the ejection of material from the reaction zone. Graphite and substrate were carefully mixed and the vial was purged with nitrogen prior to pyrolysis. Typical pyrolysis conditions are 300 °C/150W, five minutes ramp time and one minute hold time. When azulene (**1**) was pyrolyzed with graphite at 300 °C/150W under closed-vessel conditions, 60-70% was converted to naphthalene (**2**)(**Scheme 2**). [9]



Scheme 2: Isomerization of Azulene to Naphthalene [9]

This result shows that rearrangement of **1** to **2** did not occur with greater conversion with the closed vessel method. Both methods open and closed vessel, gave similar results with **2** as the only product. Sublimation of substrate from the reaction zone once again decreased the conversion to desired product. A control experiment showed that heating pure azulene without graphite under the same conditions (300 °C/150W) resulted only in sublimation of the substrate to the upper part of the tube.

We wanted to investigate the effect of temperature on the conversion of **1** to **2**. A series of experiments was conducted where temperature was varied between 100 °C and 300 °C, while maintaining the power level at 150 W (**Table 2**). At 100 °C, 34 % conversion of **1** to **2** was observed. These results support the existence of highly localized 'hot spots' with temperature higher than the bulk medium. We believe that localized heating is created by a combination of microwave absorption by the sensitizer and polarity of the substrate.

Temperature (^{o}C)	Power (W)	% conversion
300	150	65%
200	150	48%
100	150	34%

Table 2: Rearrangement of Azulene at Different Temperatures

Pyrolysis of azulene was studied with different thermal sensitizers. Finely powdered silicon carbide was investigated as a thermal sensitizer for azulene. Heating a mixture of **1** and silicon carbide for one minute at 300 °C afforded 16% conversion to **2**. The ramp time to maximum temperature was longer than with graphite, however most of the azulene sublimed out of the reaction zone. The same experiment was repeated with metal

oxides. When copper (II) oxide was used, 8% of **1** was converted to **2**. Pyrolysis with titanium dioxide resulted in 28% conversion of **1** to **2**. Although graphite was the most efficient thermal sensitizer, all of these experiments provided clean crude reactions; only starting material and product were observed by ^{1}H NMR analysis.

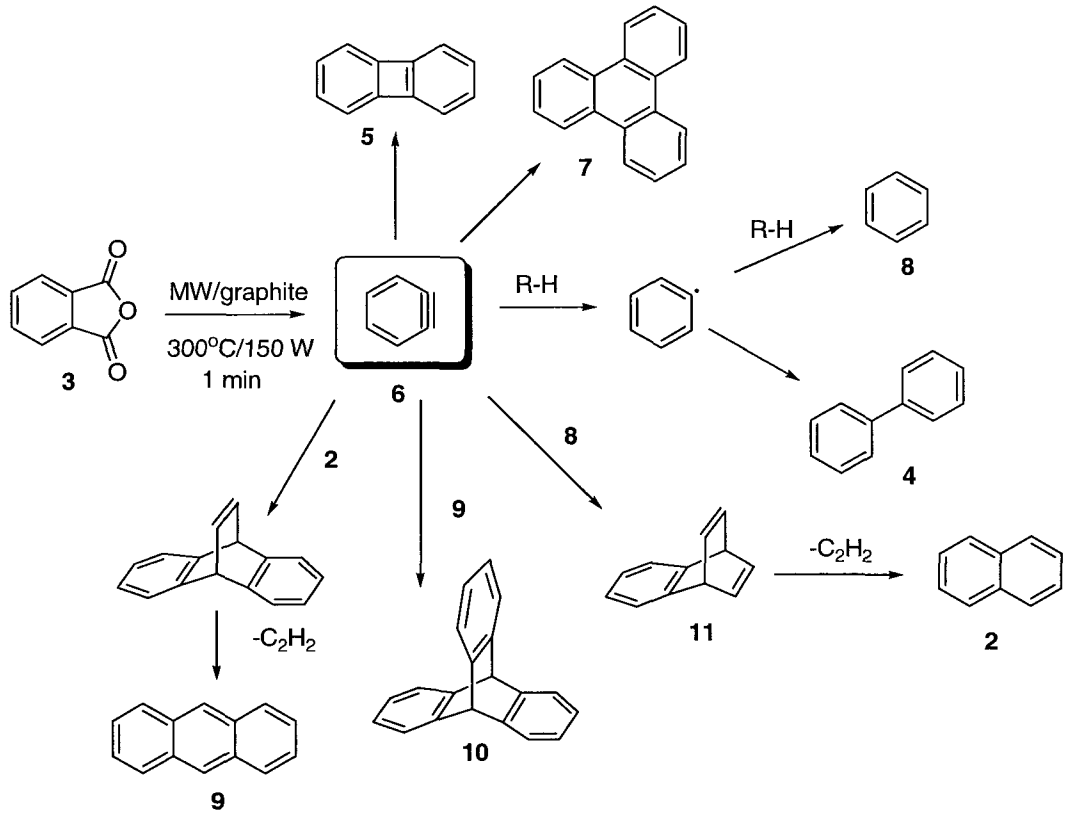
Fragmentation of Phthalic Anhydride

In 1965, Fields and Meyerson reported that thermal fragmentation of phthalic anhydride (**3**) at high temperature gives benzyne.[19,20] As reported by Friedman and Lindow, pyrolysis of phthalic anhydride in the presence of benzene yields benzyne derived products such as biphenyl, naphthalene, biphenylene and triphenylene.[21]

Fragmentation of phthalic anhydride (**3**) was first studied by Cho using the MFP open vessel approach.[13] Reaction was carried at 300 °C/300W for three one- minute periods. The crude mixture was extracted with hexanes. Initial studies showed conversion of **3** to biphenyl (**4**) as a major and biphenylene (**5**) as a minor product. A mechanism proposed by Cho[13], suggests generation of benzyne (**6**), then phenyl radical to form **4**. Initially generated benzyne leads to formation of biphenylene (**5**) through dimerization.

Cho's initial procedure was modified to improve the pyrolysis of **3**. This was accomplished by changing microwave reactor parameters and extraction solvent for the reaction. It was observed that the conversion to products improved when lower power (150 W) was used. Efficient fragmentation of phthalic anhydride is limited by sublimation when high power is used. Dichloromethane was found to be a better extraction solvent than hexane because it gave a more complete extraction. ^{1}H NMR analysis showed formation of triphenylene (**7**) as an additional product.[22]

Fragmentation of **3** was carried out using our closed vessel approach. As illustrated in Scheme 3, pyrolysis of **3** leads to formation of biphenyl (**4**, 24%) and benzene (**8**, 51%) as the major products. Low yields of biphenylene (**5**, 5%) and triphenylene (**7**, 3%) were observed by ^{1}H NMR analysis of the crude reaction mixture. These products support the observation that *ortho*-benzyne (**6**) is formed as an intermediate through loss of CO and CO_2 from **3**.[9] When a small amount of anthracene (**9**) was added to the mixture, traces of triptycene (**10**) were observed. Unexpectedly, the formation of naphthalene (**2,** 10%) was observed, which could be explained through the cycloreversion of benzobarrelene (**11**), formed through the cycloaddition of **6** and **8**. MFP of a small sample of authentic **11** produced **2** in 59% yield.[9] Another unexpected result was formation of anthracene (**9**) in 6 % yield. We hypothesized that formation of **9** results from cycloreversion of dibenzobarrelene. Dibenzobarrelene is formed through cycloaddition of **6** and **2**. MFP of authentic dibenzobarrelene resulted in 55% conversion to anthracene.



Scheme 3: Fragmentation of Phthalic Anhydride[9]

We briefly explored the pyrolysis of phthalic anhydride with silicon carbide. A mixture of **3** and silicon carbide was observed to heat slowly. Using the same reaction parameters, the same collection of products was observed in the crude mixture, with comparable ratios. Similar product distributions from sensitized pyrolysis with graphite and silicon carbide suggest that the hydrogen source in this reaction must be other molecules of substrate. This can also explain the low mass balance.

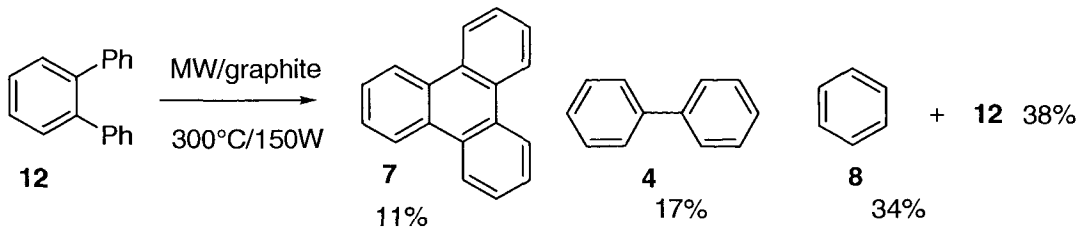
Pyrolysis in sealed tubes gave the best conversion of starting material but modest mass balance (30-40%). Benzene was one of the major products in the crude mixture which was identified by ^{1}H NMR analysis. Due to its volatility, benzene was not previously observed in the crude mixture with the open vessel method.[13]

Synthetic Routes to Polycyclic Aromatics

It has been reported that the pyrolysis of relatively simple aromatic hydrocarbons such as benzene leads to the formation of polycyclic aromatic hydrocarbons (PAHs).[23] The chemistry is believed to mimic combustion processes. These compounds have attracted significant attention not only because of their notable biological and pharmacological activity, but also because of their electrochemical and photochemical properties.[3] Through the previously described method, MFP has successfully provided a route to cycloaromatization reactions. Observed reactions include stilbene cycloaromatization, Elbs cyclizations and related reactions.[13] In the present work, we have investigated cycloaromatization of *ortho*-terphenyl and 1, 1'-binaphthyl.

Triphenylene (**7**) has been synthesized by cyclodehydrogenation of *ortho*-terphenyl and also by the Scholl reaction.[24,25] The latter often is problematic due to oligomerization of the product. MFP of *ortho*-terphenyl (**12**) with the open vessel method was first reported by Cho to give **7** in 5% yield. Cho suggested that the low solubility and low polarity of these compounds might affect the yield of isolated product.[13] The yield was improved by changing some of the microwave parameters and using more polar solvent (dichloromethane) for extraction. The mass balance of the reaction was ~ 80% and 11% of starting material was converted to **7**.[22]

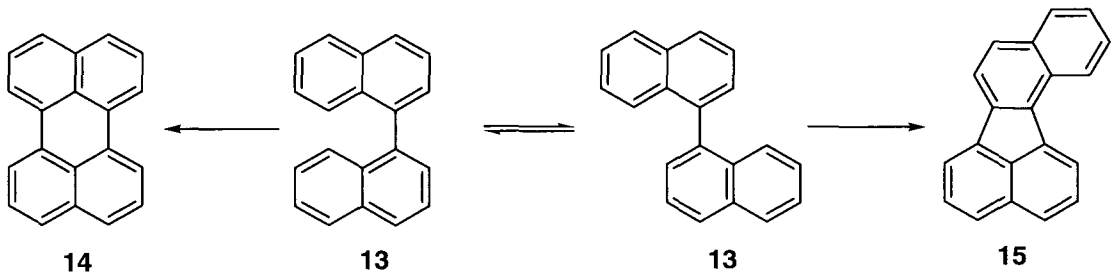
The same reaction was subjected to MFP using our closed vessel approach. As shown in Scheme 4, thermolysis of **12** with graphite at 300 °C/150W, afforded 11% of cyclized product **7**. The major products were (**4**,17%) and (**8**, 34%). Both biphenyl (**4**) and benzene (**8**) were not observed via open vessel MFP. This demonstrates the advantage of the closed vessel method to capture all volatile reaction products.



Scheme 4: Thermolysis of *ortho*-Terphenyl

We briefly explored different metal oxides as thermal sensitizers. When pyrolysis was carried out with tungsten oxide, 14% of cyclized product **7** was observed. Pyrolysis with copper (II) oxide afforded 1.5% of **7**. The pyrolysis with CuO resulted mostly in sublimation of the substrate from the hot zone. The results from the pyrolysis with WO_3 yielded higher conversion of starting material and the product distribution was comparable to those with graphite.

1, 1'-Binaphthyl (**13**) is an interesting substrate because cycloaromatization can proceed in two directions to give either perylene (**14**) or benz[j]fluoranthene (**15**) (**Scheme 5**).

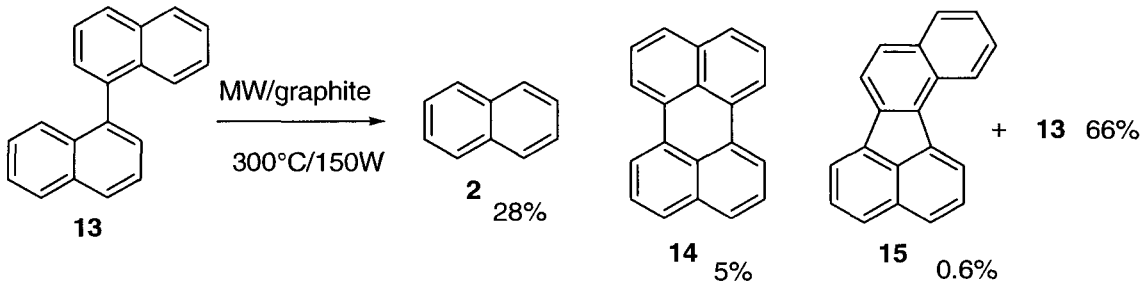


Scheme 5: Cycloaromatization of 1, 1'- Binaphthyl

One of the ways to prepare **14** is by catalytic cyclodehydrogenation of **13**.[26] Our attempt was to synthesize **14** from **13** using MFP. The initial pyrolysis of **13** was investigated using the open vessel approach. When **13** was pyrolyzed with graphite at 300

°C/150W, only 3% of starting material was converted to **14** and 27% was converted to **2**. Benz[j]fluoranthene (**15**) was also generated in a very low yield of 0.5 %. [22]

Sealed tube pyrolysis of 1, 1'-binaphthyl (**13**) with graphite at 300 °C/150W gave the expected cyclized products, **14** (5%) and **15** (0.6%). However, the major product was **2,** formed in 28% yield (**Scheme 6**). The dominant formation of **2** in this reaction is highly unusual and was unexpected. Based on B3LYP/G-31G* energies, the σ bond dissociation energy of **13** was estimated to be 111.6 kcal/mol. The cleavage of this strong sigma bond demonstrates the power of MFP.

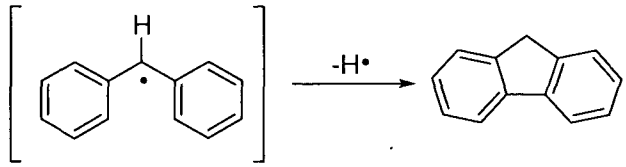


Scheme 6: Pyrolysis of 1, 1'-Binaphthyl

We conclude that cycloaromatization is the minor process in MFP of both **12** and **13**. The limitation to the cyclization pathway appears to be the sublimation of starting material from the hot zone. The major products in both cases resulted from the cleavage of the aryl-aryl bond.

Thermal Routes to Five-Membered Rings

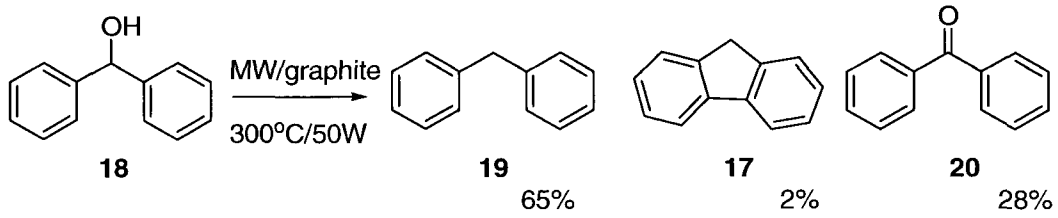
There has been much recent interest in the synthesis of bowl-shaped polycyclic aromatic hydrocarbons. [27,28] It is well recognized that five membered rings are the key structural features that determine a nonplanar molecular geometry.[29] The present work was undertaken with the goal of developing a novel thermal route to five membered rings based upon the cyclization of diphenylmethyl radical (**16**) to fluorene (**17**) (**Scheme 7**).



Scheme 7: Diphenylmethyl Radical as a Precursor to Fluorene

Initial approach was to carry out pyrolysis of benzhydrol (**18**) using an open vessel MFP method. It was hypothesized that this substrate would undergo cleavage of the hydroxyl radical to yield the desired diphenylmethyl radical, which would give **17**. Open vessel pyrolysis of **18** was carried out with graphite at 300 °C/150W. ^{1}H NMR analysis of the crude mixture showed formation of diphenylmethane (**19**) as the major product. We also observed formation of fluorene and benzophenone (**20**) as minor products. It was difficult to determine the percent yield of each component in the crude mixture due to the overlapping chemical shifts in the mixture. [22]

Pyrolysis of benzhydrol was investigated using the closed vessel MFP approach. As illustrated in Scheme 8, pyrolysis of **18** at 300 °C/50W afforded 65 % of **19**, 2 % of **17** and 28 % of **20**.

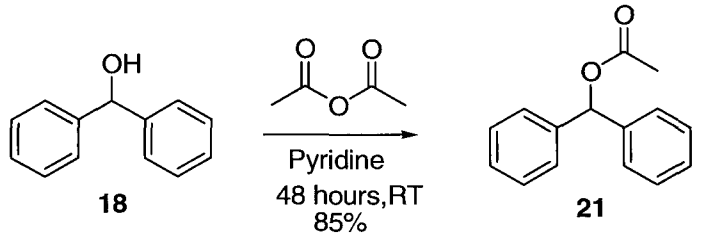


Scheme 8: Pyrolysis of Benzhydrol

The percent yield of each component in the mixture was determined by analytical GC analysis. Starting material was not observed. ^{1}H NMR analysis of the crude mixture confirmed formation of the major and minor components in the mixture. These results

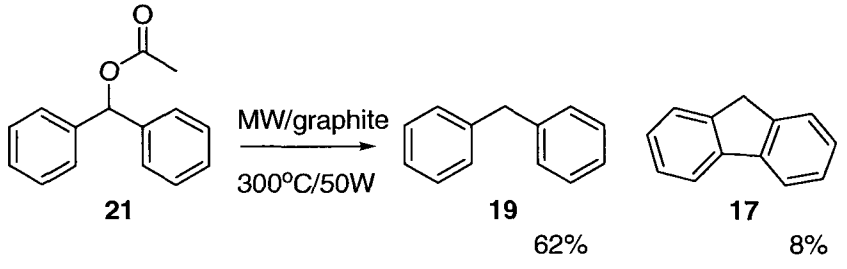
support the formation of diphenylmethyl radical, but instead of undergoing cyclization to give **17** this yielded primarily **19** by abstracting a hydrogen.

To improve the previous route to **17** by providing a more easily broken bond, we investigated pyrolysis of diphenylmethylacetate (**21**). In addition, this substrate should not give **20**. Prior to carrying out the pyrolysis, **21** was synthesized by acylation of **18** (**Scheme 9**).



Scheme 9: Synthesis of Diphenylmethylacetate

Pyrolysis of **21**was carried out in a sealed tube with graphite at 300 °C/50W. The crude mixture was extracted with dichloromethane, concentrated and analyzed with ^{1}H NMR. Capillary GC analysis was carried out to determine the percent yield of each component in the mixture.

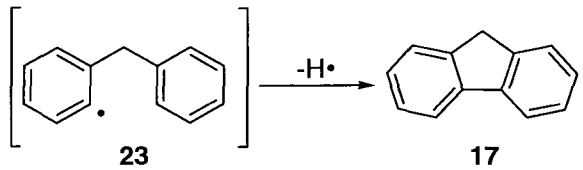


Scheme 10: Pyrolysis of Diphenylmethyl Acetate

As indicated in Scheme 10, pyrolysis of diphenylmethylacetate gives 62 % of **19** and 8% of **17**. The remaining component in the mixture was the starting material. This route improved conversion to fluorene, but diphenylmethane remained a major product.

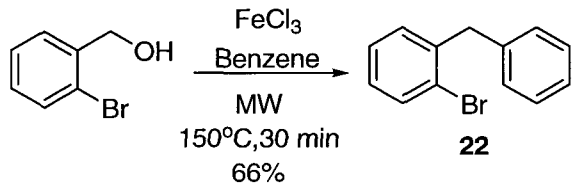
Both substrates under study gave the desired five-membered product as the minor and diphenylmethane as the major product. Although formation of fluorene is evident, a diphenylmethyl radical might not be the best precursor to five-membered rings.

We investigated a third approach to thermally synthesize **17**. This route used 1-benzyl-2-bromobenzene (**22**) as a precursor to phenyl radical (**23**) and subsequently **17**.



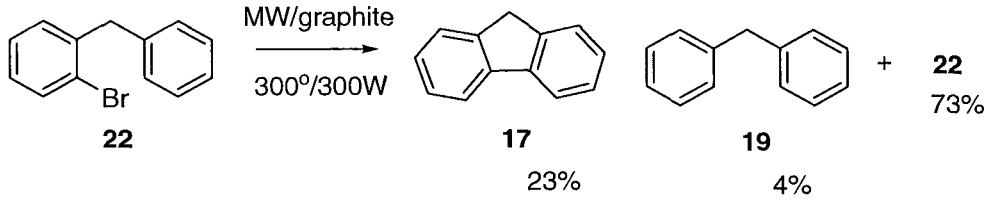
Scheme 11: Phenyl Radical as a Precursor to Fluorene

Starting material was synthesized prior to pyrolysis via electrophilic aromatic substitution reaction (**Scheme 12**). This reaction has been reported previously by conventional reflux.[30] We observed that microwave conditions are more efficient.



Scheme 12: Synthesis of 1-Benzyl-2-bromobenzene

Initial pyrolysis of **22** was carried out in a sealed tube at 300 °C/300W. The crude mixture was analyzed by GC (**Scheme 13**) and was composed of **17** (23%), **19**(4%) and **22** (73%). Given this modest conversion, we decided to repeat the reaction using lower a power level to increase conversion to the desired product. Our rationale for this change is that high power promotes sublimation rather than a reaction.



Scheme 13: Pyrolysis of 1-Benzyl-2-bromobenzene

When **22** was subjected to pyrolysis at 300 °C/50W and analyzed by GC, **17** was formed in 37% yield. The crude mixture contained **19** (7%) and starting material (50%). Changing the power level to 50 W resulted in a slightly higher conversion of **22** to **17** (41%). However, even with this low power the starting material was still present in a high concentration. It may be possible to optimize product yield by further variations in reaction conditions.

We investigated the FVP of **22**. When **22** was subjected to FVP at 800 °C, only 10% of starting material was converted to **17**. The crude mixture contained only starting material and **17** as determined by ^{1}H NMR and GC. ^{1}H NMR data agreed with those reported in the literature. Increasing the temperature above 800 °C may perhaps improve conversion of starting material to desired product.

A photochemical route to fluorene was explored with **22** as a starting material. The reaction was run for 24 hours with *tert*-butyl alcohol as solvent. GC analysis of the crude mixture confirmed formation of **17** (14%) and **19** (33%). The only hydrogen source in the reaction mixture was *tert*-butyl alcohol.

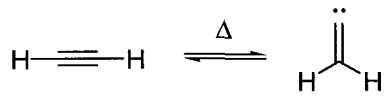
These experiments demonstrate a modestly efficient MFP route to five-membered rings. The best conversion of starting material to fluorene was achieved with low power pyrolysis. FVP resulted in a low yield of desired product, due to a low volatility of the substrate. This shows that MFP method offers the advantage for nonvolatile substrates.

CHAPTER II

THERMAL REARRANGEMENTS

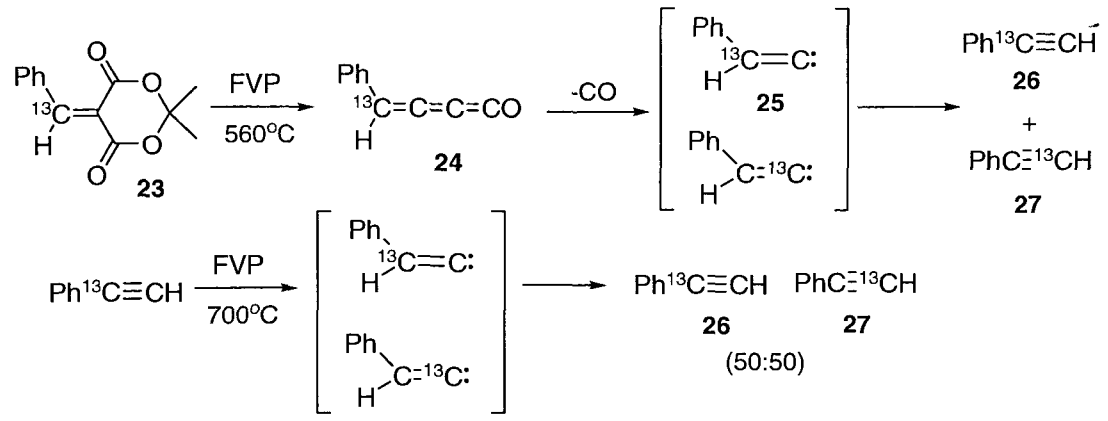
Introduction

The thermal interconversion of alkynes and vinylidenes, also known as the Brown rearrangement, is a reaction that is important synthetically and mechanistically (**Scheme 14**).



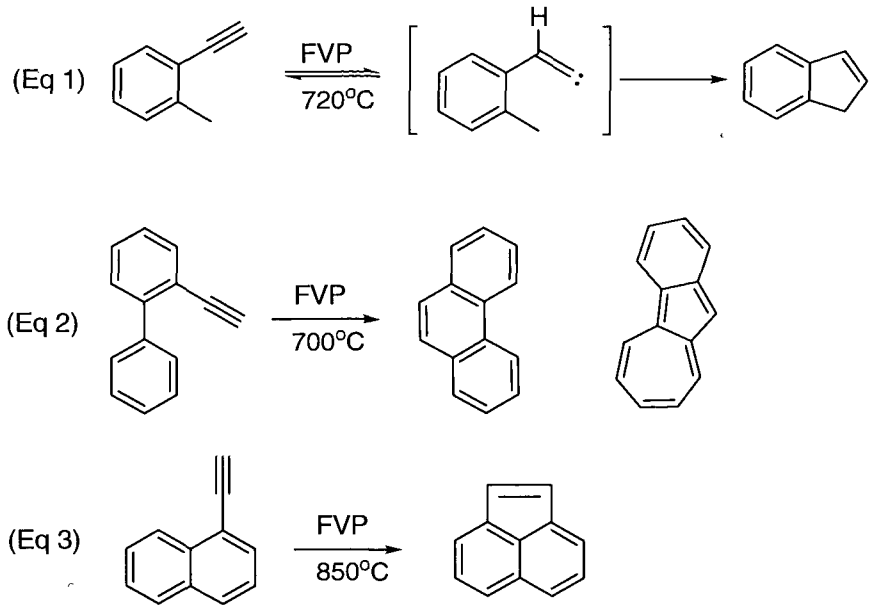
Scheme 14: The Brown Rearrangement

Brown and coworkers began studying acetylenic chemistry in 1972 with the generation of cumulenones, which were not known at the time. Pyrolysis of ^{13}C labeled isopropylidene benzylidenemalonate (**23**) at 560 °C resulted in formation of cumulenone **24**. Decarbonylation of this structure yielded phenylacetylene isotopomers which were believed to result from vinylidene intermediate **25**. Pyrolysis of a single phenylacetylene isotopomer at 700 °C gave a 50:50 mixture of **26** and **27** (**Scheme 15**). This was the first evidence of a high temperature equilibrium between acetylenes and vinylidenes.[31,32]



Scheme 15: Equilibration of Acetylene and Vinylidene

Many applications of the Brown rearrangement have been described[33,34](**Scheme 16**). Generation of a carbene next to a substituent bearing C-H bonds presentes the possibility of insertion reactions to form fused polycyclic hydrocarbons. An intramolecular insertion reaction was evident in the pyrolysis of 2-ethynyltoluene at 720 °C, leading to indene as the major product (**Eq 1**). Pyrolysis of 2-ethynylbiphenyl at 700 °C (**Eq 2**) gives the vinylidene which undergoes C-H insertion to give phenanthrenes. The vinylidene also adds into the π system of the adjacent phenyl substituent and then rearranges to yield benz[a]azulene. [31,32] Pyrolysis of 1-ethynylnaphthalene led to carbene C-H insertion to give acenaphthalene (**Eq 3**). These reactions demonstrate the scope of carbene cyclizations that can be utilized in synthesis of higher polycyclic hydrocarbons.



Scheme 16: Reactions Reported by Brown *et al.*[32]

Project Goals

With a development of the sealed tube pyrolysis, we sought to explore the limitations of MFP. The work started with the investigation of the Brown rearrangement, one of the most common high temperature thermal reactions. The question we posed was if this rearrangement would occur under MFP conditions. The preliminary work focused on several well known structures, specifically 2-ethynylbiphenyl and 2-ethynyltoluene.

Theory played a major role in this work. Earlier studies by Mackie and Johnson[35] supported the experimental work. Recent theoretical studies by Voukides[36] promoted the investigation of thermal rearrangements and led to further understanding of the mechanisms.

As the project evolved, we designed new experiments to help understand the mechanistic complexity that we discovered. Formation of chrysene through an allene intermediate was of interest and it was investigated thoroughly. In addition, a synthesis of

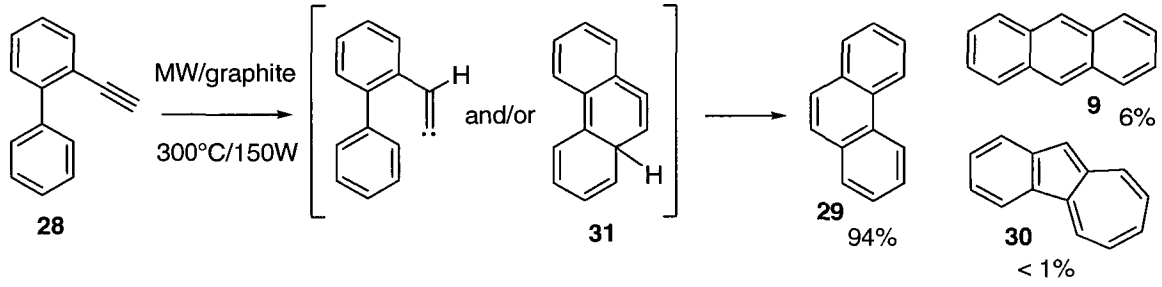
initial structures that favor [1, 5] hydrogen shift, to give *ortho*-xylallene intermediate, was attempted to facilitate formation of higher polyacenes.

Results and Discussion

Thermolysis of 2-Ethynylbiphenyl

In 1974, Brown and co-workers showed that FVP of 2-ethynylbiphenyl (**28**) at 700 °C gives phenanthrenes (**29**) and benz[a]azulene (**30**) in a 72:28 ratio.[32] The mechanism for product formation begins with 1,2-shift to form a carbene intermediate, which then inserts into adjacent C-H or C=C bonds to give the two observed products.

2-Ethynylbiphenyl (**28**) was easily prepared by palladium catalyzed Sonogashira coupling of 2-bromobiphenyl with trimethylsilylacetylene, followed by removal of the TMS group.[37] Thermal rearrangement of **28** was investigated via MFP using our closed vessel approach (**Scheme 17**). When **28** was pyrolyzed with graphite at 300 °C/150W for one minute hold time, the major products were **29** (94%) and **9** (6%). Traces of **30** (< 1%) were observed by ^{1}H NMR analysis of the crude reaction mixture. Formation of **9** was unexpected, but this can be explained as a secondary product of **30**.



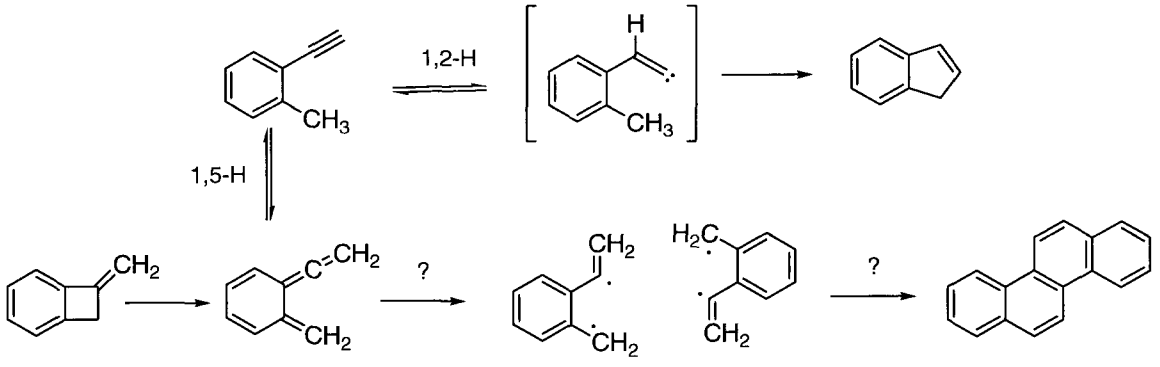
Scheme 17: Rearrangement of 2-Ethynylbiphenyl

In 1975, Whittaker and Alder reported that the pyrolysis of **30** affords **29** and **9** in a 2.5:1 ratio.[16] These earlier results provide evidence that the primary products are **29** and **30**, and **9** is a secondary product of **30**. This is another example of the Brown

rearrangement; however, Mackie and Johnson showed via computational studies that there is a competitive pathway to **29** through cyclic allene **31**. [35]

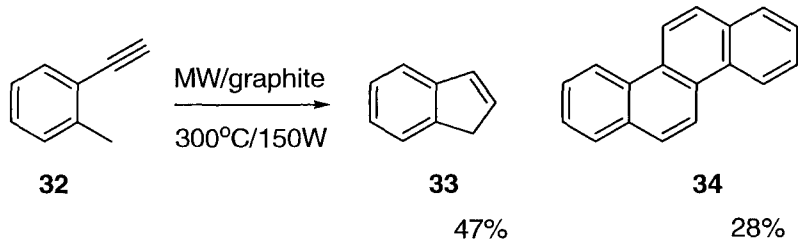
Thermolysis of 2-Ethynyltoluene

In 1974, Brown *et.al*[32] reported that FVP of 2-ethynyltoluene at 720 °C gave a mixture of indene (78%) and chrysene (1%). Brown and coworkers speculated that formation of chrysene comes from dimerization of an "allene diradical" followed by dehydrogenation (**Scheme 18**). Another possible route to the allene intermediate, reported by Brown, would be from methylenebenzocyclobutene. When this compound was subjected to pyrolysis, only indene and 2-ethynyltoluene were observed.



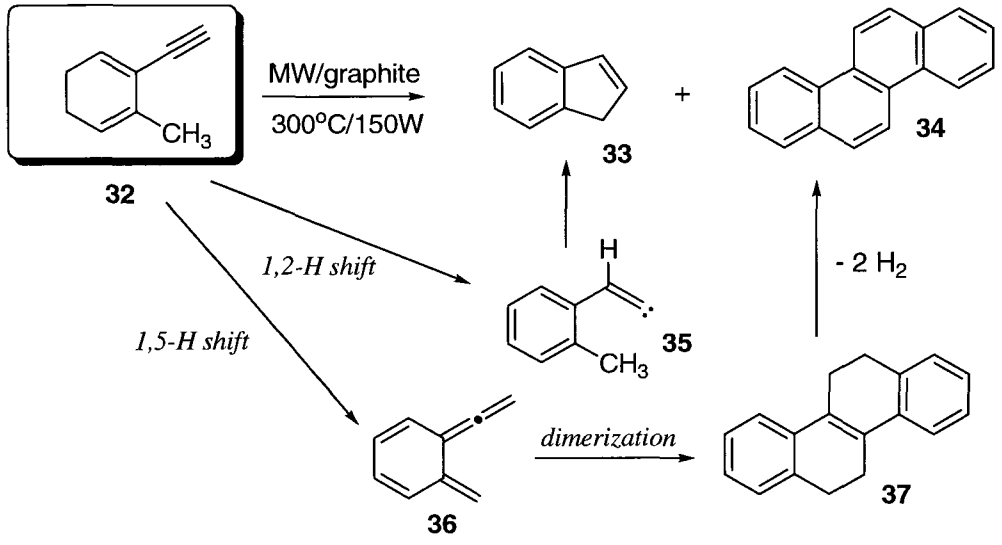
Scheme 18: Mechanism Proposed by Brown *et al.* for the Conversion of 2-Ethynyltolune[32]

Initially, we subjected the same reaction to MFP (**Scheme 19**), and found that 2-ethynyltoluene (**32**) was converted primarily to indene (**33**,47%) and chrysene (**34**,28%). This is a significant result because MFP reactions are run in several minutes, whereas FVP takes several hours for reactions because of the more complex set up and initial heating. The dramatic increase in our yield of **34** is also noteworthy.



Scheme 19: Thermolysis of 2-Ethynyltoluene

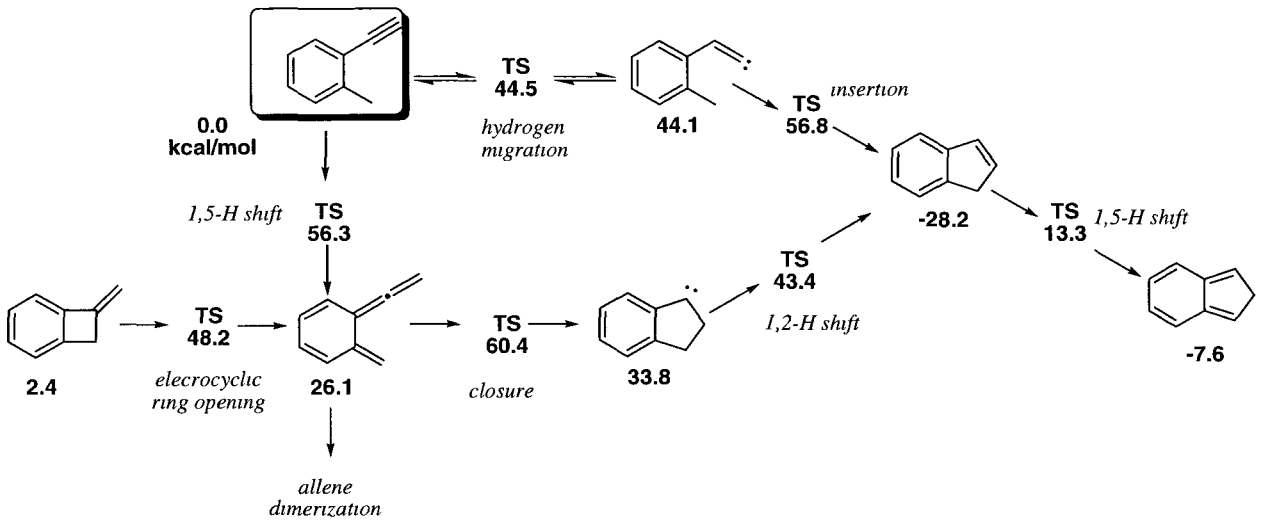
As illustrated in Scheme 20, these reaction products indicate a competition between 1,2-hydrogen shift, also known as the Brown rearrangement, to give vinylidene **35** and 1,5-hydrogen shift to give *ortho*-xylallene (**36**). Intermediate **35** undergoes C-H insertion to give **33**, while intermediate **36** undergoes dimerization to give **37**, followed by dehydrogenation to give **34**. Our sealed tube pyrolysis increased the yield of **34**, presumably due to a high transient concentration of *ortho*-xylallene (**36**).



Scheme 20: Thermal Rearrangement of 2-Ethynyltoluene

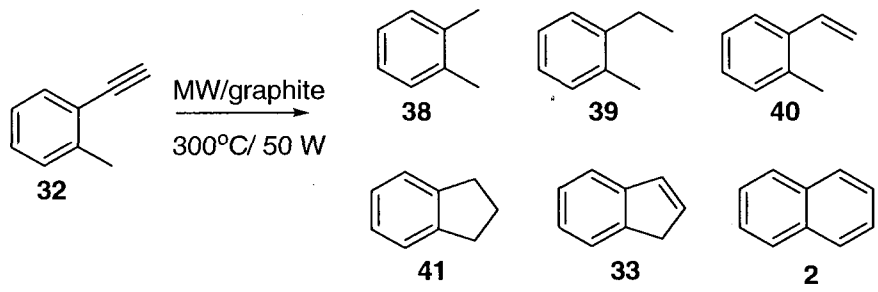
The computational studies for this reaction were done by Voukides in our group. DFT calculations (**Scheme 21**) support the competition between 1,2 and 1,5- hydrogen shift. [36] Since the 1,2-hydrogen shift is fast and reversible, the rate determining step is the C-H insertion that follows 1,2-hydrogen shift. This insertion competes with the 1,5-

hydrogen shift, both of which have comparable barriers at approximately 56 kcal/mol. Another possible route to *ortho*-xylallene is electrocyclic ring opening of methylenebenzocyclobutene.



Scheme 21: CCSD(T)/6-311G(d)//B3LYP/6-311+G(d,p) Energetics for the Thermal Rearrangement of 2-Ethynyltoluene

More detailed studies revealed the presence of minor products that may help explain reaction mechanisms. MFP of **32** was carried out with graphite (1:2 ratio) at 300 °C/ 50W for five minutes reaction time. The crude mixture was extracted first with pentane to remove low molecular weight products, followed by dichloromethane extraction to capture high molecular weight products. The pentane extract was separated by preparative GC (122 °C), yielding the following products in order of elution (**Scheme 22**): o-xylene (**38**,14%), 2-ethyltoluene (**39**,11%), 2-vinyl toluene (**40**,7%), indan (**41**,10%), and indene (**33**,34%).



Scheme 22: Components in the Pentane Extract

Percentages were determined by cutting and weighing peaks on the chromatogram (**Figure 1**). ^{1}H NMR analysis confirmed the identity of each component. In addition, traces of naphthalene (**2**) were observed in the pentane extract by ^{1}H NMR analysis. The dichloromethane extract was analyzed by ^{1}H NMR, showing this to be primarily chrysene. There were additional compounds (PAH's) present in the extract which were observed by ^{1}H NMR and TLC analysis. Formation of **2** was unexpected and therefore the pyrolysis was repeated and more detailed analysis of the pentane extract was completed.

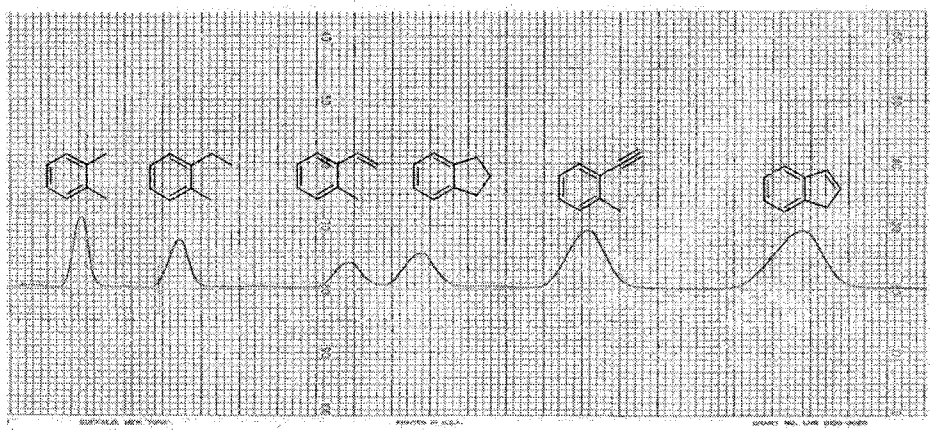


Figure 1: Chromatogram of the Components in the Pentane Extract

Pyrolysis was carried out using 1:2 ratio of substrate to graphite at 300 °C/ 50W for five minutes. The pentane extract was analyzed by capillary GC, showing the following products in order of elution: **38** (6%), **39** (5%), **40** (4%), **41** (10%), **33** (30%),

and **2** (27%). Separation of the pentane extract was completed via preparative GC (122 °C). All fractions were analyzed by ^{1}H NMR and identified by comparison to authentic samples. Naphthalene was not separated by preparative GC, even after increasing the column temperature (150 °C). Therefore, the formation of naphthalene was solely observed by ^{1}H NMR and capillary GC. Once again, ^{1}H NMR analysis of the dichloromethane extract showed chrysene as major and additional PAH's as minor products. The components in the mixture have very similar R_f values, and an attempt to separate them by preparative TLC or radial TLC was not successful. From ^{1}H NMR analysis (**Figure 2**), the crude mixture contained chrysene (**34**) and its isomers, benzo[a]anthracene (**42**) and benzo[c]phenanthrene (**43**) in a ratio of 71:23:6. Pyrolysis of **34** under the same conditions does not give **42** and **43**; only starting material is observed by capillary GC and ^{1}H NMR analysis.

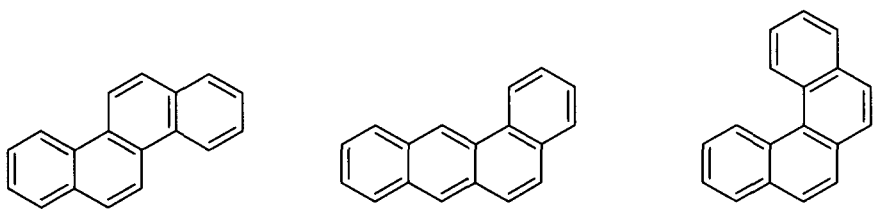


Figure 2: Components in Dichloromethane Extract

To explore the effect of MW power on the product distribution, pyrolysis of **32** was repeated with graphite (1:2 ratio) at 300 °C/ 150W for five minutes ramp time and one minute hold time. A standard procedure was followed and both pentane and dichloromethane extracts were subjected to analysis. The pentane extract was analyzed via capillary GC and yielded the following products in order of elution: **38**(14%), **39** (16%), **40** (7%), **41** (12%), **33** (23%), **2** (6%), and **32**(16%). ^{1}H NMR analysis of the dichloromethane extract showed a mixture of **34** and its isomers **42** and **43**.

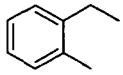
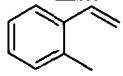
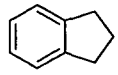
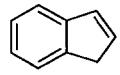
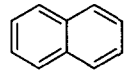
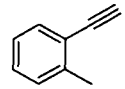
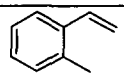
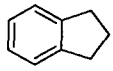
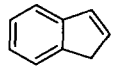
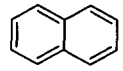
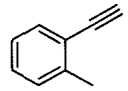
MW Parameters	 38	 39	 40	 41	 33	 2	 32
300°C/50W	6%	5%	4%	10%	30%	27%	19%
300°C/150W	14%	16%	7%	12%	23%	6%	16%

Table 3: Pyrolysis of 2-Ethynyltoluene at 50W and 150W

Table 3 illustrates the product distribution when varying MW power (50 and 150 W). These experiments demonstrate that a higher conversion of substrate to indene was observed at 50W (**Table 3**). Overall the conversion of substrate to products is slightly higher when lower power is used.

We next explored the effect of concentration on the product distribution. It was hypothesized that low concentration of substrate to graphite would diminish bimolecular chemistry. Three experiments were conducted in which the amount of graphite was constant (50 mg) and the amount of substrate was varied from 10, 20, and 30 mg. All experiments were carried out at 300 °C/ 150W and the crude mixture was extracted with dichloromethane, concentrated, and subjected to ^{1}H NMR and GC analysis.

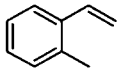
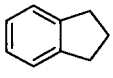
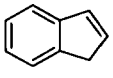
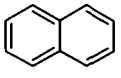
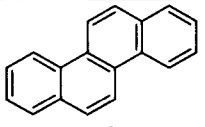
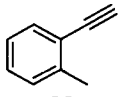
As illustrated in Table 4, at low substrate concentration the major product was **33** (69%). Formation of **2** was also observed (8%). As the substrate concentration increases, **33** appears to be the major product and additional minor products are being formed. Minor products appear to be secondary products of **33**. The yield of **2** diminishes as the concentration of substrate increases. At high substrate concentration, **2** was not detected by capillary GC analysis. However, ^{1}H NMR analysis showed that traces of **2** were present in the crude mixture.

Reactants [a]	 40	 41	 33	 2	 32
10/50	x[b]	x[b]	68	8	24
20/50	4	5	64	4	23
30/50	7	6	40	x[c]	35

a) mg of substrate / mg of graphite b) X=not detectable c) See text; Note: The numbers indicate the % of isolated product

Table 4: Pyrolysis of **32**: Product Distribution from Capillary GC Analysis at Variable Concentrations

It is evident from these experiments that the MW power and the concentration of substrate affect the product distribution. With that in mind, we decided to investigate how the product distribution changes with time. Experiments were carried out at 300 °C/50W. The lower concentration of substrate to graphite (1:5 ratio) was utilized to diminish secondary reactions. The experiments were conducted at 1, 2, 3.5 and 5 minutes pyrolysis time. The crude mixture was extracted with dichloromethane, filtered, concentrated and analyzed by ^{1}H NMR and capillary GC.

Total Time (min)	 40	 41	 33	 2	 34	 32
1	x[a]	2	53	5	10	30
2	1.6	2	49	4	11	33
3.5	1.6	1.9	44	3	8	38
5	2	3	53	4	12	26

a)X=not detected; Note: The numbers indicate the % of isolated product

Table 5: Pyrolysis of **32**: Product Distribution from Capillary GC analysis at Variable Reaction Times

These results show that very short reaction time (one minute) is sufficient to convert >70% of **32** to products. As illustrated in Table 5, the major product in all reactions is indene (**33**). Formation of **2** and **34** was observed in the crude mixture. The

percentage of indene and other products changes only slightly with time. Indene, the primary product of pyrolysis, is being converted to secondary products **40** and **41**, with time.

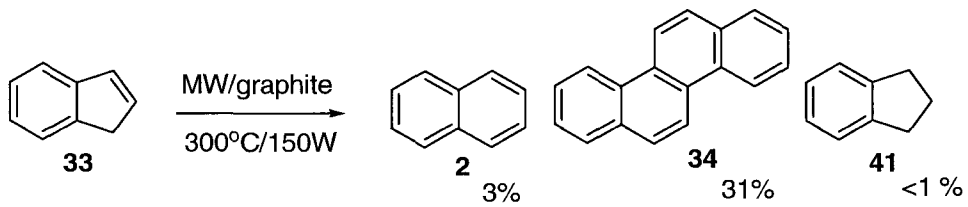
MFP of **32** thus gives a very complex mixture of products. There are primary and secondary products formed in this reaction and their ratios vary with the reaction parameters. We have investigated the effects of the MW power level, concentration and time on the product distribution. Indene is a primary product and other minor products appear to be secondary products of indene. Indan (**41**) is formed upon addition of hydrogen atoms to **33**. The hydrogen source in the reaction may be tetrahydrochrysene which is a precursor to **34**.With lower concentration and shorter reaction times, secondary products are less likely to be formed.

Formation of naphthalene diminishes with increased concentration. At lower concentration more naphthalene is formed but its yield does not change as the reaction time is increased. It is postulated that naphthalene is generated from a reaction of indene with an atomic carbon. It is known that indene yields to naphthalene if reacted with atomic carbon.[38]We have suggested that the source of atomic carbon in our reactions is graphite. We did a control study in which indene is subjected to MFP with graphite and one of the products is indeed naphthalene. This chemistry will be explained later in the chapter. Chrysene is believed to be formed through dimerization of *ortho*-xylallene which arises via 1,5-hydrogen shift from **32**. According to computational studies done by Voukides[36], the dimerization is driven by its substantial exothermicity. These results show clearly that, with MFP, we are generating high concentrations of reactive intermediates, which allows for bimolecular processes to result in complex mixtures.

Pyrolysis of Indene

The results described above led us to investigate the MFP chemistry of indene. Pyrolysis of liquid indene (**33**) was first reported in 1893 by Spilker *et al.* to give chrysene(**34**) as the major product.[39] In 1960, Badger *et al.* reported that pyrolysis of **33** gives **34** and other polycyclic aromatic hydrocarbons.[23,40] They postulated that **34** is formed through dimerization of two diradicals which arise bond scission in indene. Here, we study pyrolysis of **33** via MFP with graphite.

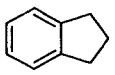
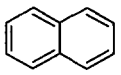
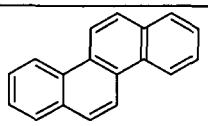
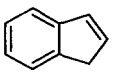
Pyrolysis of **33** was investigated with our closed vessel method. The reaction was first carried out with graphite at 300 °C/150W and reaction times of one to five minutes. The crude mixture was extracted with dichloromethane, filtered, concentrated and analyzed by ^{1}H NMR and GC. ^{1}H NMR analysis of the crude mixture confirmed the formation of **34** as the major and **2** as a minor product. A small amount of indan (**41**) was observed by ^{1}H NMR analysis of the crude mixture. In addition, traces of benzo[a] anthracene (**42**) and benzo[c] phenanthrene (**43**) were observed in the crude mixture. The characterization was done by comparing observed chemical shifts to the reported chemical shifts in the literature.[41,42] According to GC analysis (**Scheme 23**), the crude mixture was composed of **33** (60%), **2** (3%), and **34** (31%).



Scheme 23: Pyrolysis of Indene

It was demonstrated earlier with 2-ethynyltoluene (**32**) that conversion to products occurs in a short reaction time. From a one minute reaction, we observed 53% conversion

of **32** to indene. For that reason, we investigated the pyrolysis of **33** utilizing different reaction times. Pyrolysis of **33** was carried out at 300 °C/50W for 1, 2, 3.5 and 5 minutes. The experiments were carried out at low concentration of substrate to graphite (1:5 ratio) to diminish bimolecular reactions.

Total Time (min)	 **41**	 **2**	 **34**	 **33**
1	2	1	12	83
2	3	2	13	82
3.5	3	2	19	76
5	3	3	22	71

Note: The numbers indicate the % of isolated product

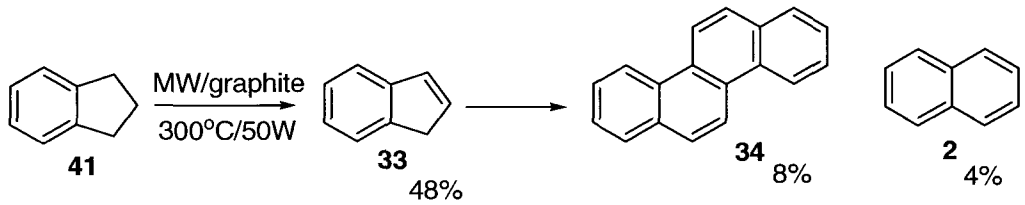
Table 6: Pyrolysis of **33**: Product Distribution from Capillary GC analysis at Variable Reaction Times

As illustrated in Table 6, pyrolysis of **33** gives **34** as the major product. Significant quantities of starting material are present in the crude mixture, presumably due to boiling out of the reaction zone. At longer reaction times, the percent of **34** increases, but the percentage of other components in the mixture does not change significantly.

We briefly explored pyrolysis of indene with multi-walled nanotubes (MWNT). Closed tube pyrolysis of **33** was carried out at 300 °C/50W. The crude mixture was extracted with dichloromethane, filtered, concentrated and analyzed by capillary GC and ^{1}H NMR. Capillary GC analysis indicated following product distribution: indan (**41**, 20%), naphthalene (**2**, < 1%), and chrysene (**34**, 8%). This result indicates that MWNTs may perhaps be a hydrogen source leading to **41** as a major product. Given that traces of

2 are observed, we can rationalize that MWNTs may possibly be a source of atomic carbon at high temperatures, but they are not as efficient as graphite.

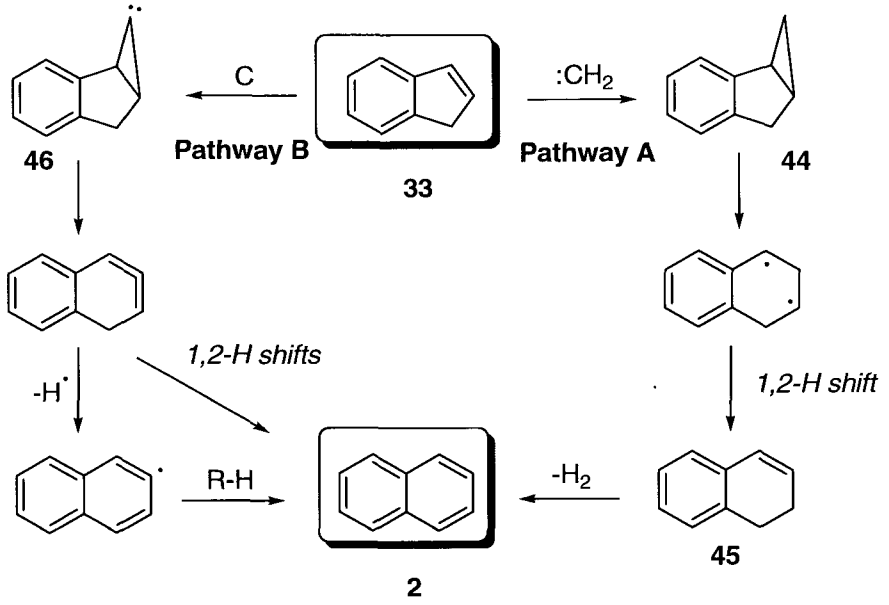
Pyrolysis of indan (**41**) was investigated to better understand the mechanism of the reaction and product distribution. The pyrolysis was carried out under standard MFP conditions, 300 °C/50W for five minutes. The crude mixture was extracted with dichloromethane, filtered, concentrated and analyzed by ^{1}H NMR and capillary GC. Capillary GC analysis (**Scheme 24**) showed that pyrolysis of **41** gives **33** (48%), **2** (4%) and **34** (8%). The primary product in this reaction is **33** which reacts further to give **2** and **34** as secondary products. This is consistent with our previous results.



Scheme 24: Pyrolysis of Indan

It was first suggested by Brown that compound **34** is formed through dimerization of an *ortho*-xylallene intermediate. As mentioned earlier, **2** is a likely product of **33** and atomic carbon. The source of atomic carbon is believed to be graphite. Investigation to confirm that graphite is indeed a source of atomic carbon is continuing. Here we propose two mechanistic pathways for the formation of **2** from **33** (**Scheme 25**). Pathway A involves reaction of **33** with methylene (H_2C:), which may perhaps come from another molecule present in the mixture, to give **44**. Cleavage of the cyclopropane bond in **44** gives 1,3-diradical species[43,44] which undergoes 1,2-hydrogen shift to give 1,2-dihydronaphthalene (**45**) and subsequently **2**. Pyrolysis of **44** has been reported previously to give naphthalene, in addition to 1,2- and 1,4-dihydronaphthalenes.[43]

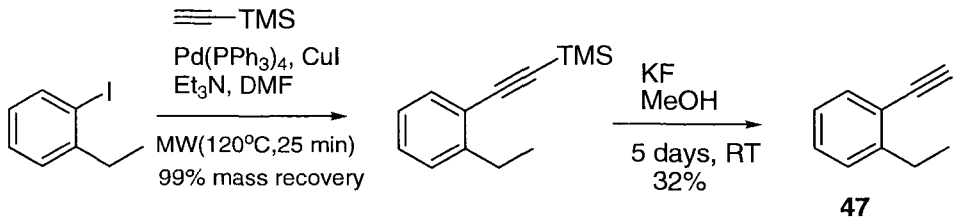
Pathway B describes reaction of **33** with atomic carbon to yield naphthalene. This was reported previously by Shevlin.[45] The mechanistic pathway involves formation of cyclopropylidene **46** which undergoes ring opening to a cyclic allene, followed by sequential 1,2-hydrogen shifts to yield **2**. The cyclic allene can also undergo hydrogen radical loss to give naphthyl radical and then naphthalene.



Scheme 25: Proposed Mechanistic Pathways for the Formation of Naphthalene

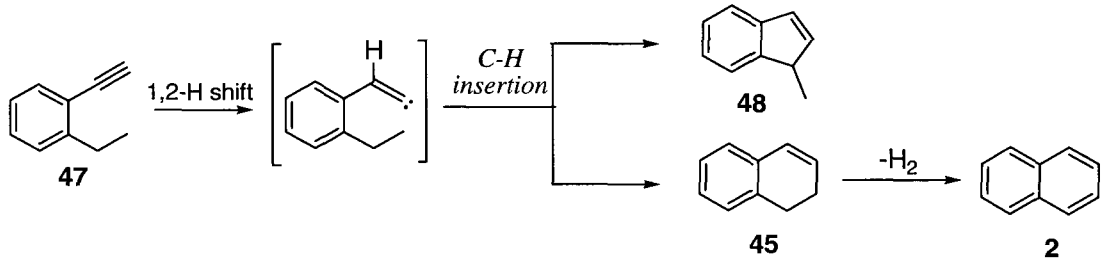
Thermal rearrangement of 1-Ethynyl-2-Ethylbenzene

The investigation of aryl alkyne rearrangements was continued with 1-ethynyl-2-ethylbenzene (**47**). Prior to carrying out MFP, 1-ethynyl-2-ethylbenzene (**47**) was synthesized via a two step method, seen in Scheme 26. The synthetic route utilizes palladium catalyzed Sonogashira[37] coupling of 1-ethyl-2-iodobenzene with trimethylsilylacetylene, followed by removal of the TMS group.



Scheme 26: Synthetic Pathway to 1-Ethynyl-2-ethylbenzene

Pyrolysis of **47** was investigated. It was hypothesized that when subjected to pyrolysis, **47** would lead to formation of 1-methylindene (**48**) and 1,2-dihydronaphthalene (**45**). 1,2- Dihydronaphthalene (**45**) is expected to aromatize easily to afford naphthalene (**2**). As illustrated in Scheme 27, these two products would result from 1,2-hydrogen shift to give the vinylidene intermediate, followed by two different C-H insertion pathways. According to computational studies done by Voukides in our group, the C-H insertion pathway to give **48** should be favored relative to formation of **45.**[36]

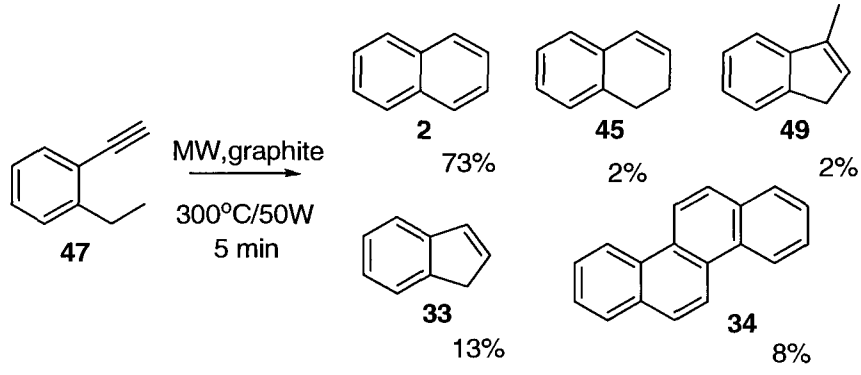


Scheme 27: Proposed Route to 1-Methylindene and 1,2-Dihydronaphthalene

Initial MFP of **47** was carried out at 300 °C/150 W for a one minute reaction time. The crude mixture was extracted with pentane, followed by dichloromethane extraction. ^{1}H NMR analysis of the concentrated pentane extract showed that naphthalene (**2**) was formed as the major product. Minor products in the pentane extract were indene (**33**) and 3-methylindene (**49**). Traces of 1,2-dihydronaphthalene and 2-methylindene were also observed in the crude mixture. Separation of the crude mixture by preparative GC was carried out. All components in the mixture could be separated except for methylindene

isomers. They have the same retention times and therefore can not be isolated separately. Percentages of major and minor components in the mixture were determined by capillary GC. The characterization was completed by comparison of retention times of the components in the mixture with the retention times of pure compounds. ^{1}H NMR analysis of the dichloromethane extract confirmed the formation of chrysene. Formation of indene (**33**) and chrysene (**34**) was unexpected, therefore we decided to optimize the conditions and repeat the pyrolysis.

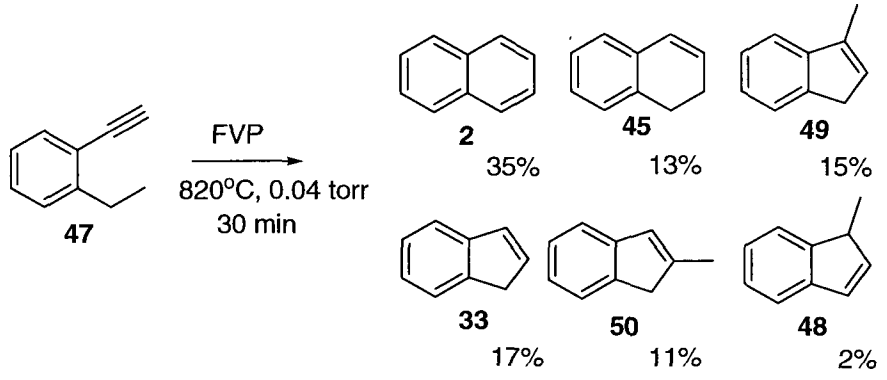
Closed tube pyrolysis was repeated at lower power and lower concentration of substrate to graphite (1:5). The crude mixture was extracted with dichloromethane and analyzed by ^{1}H NMR and capillary GC. As illustrated in Scheme 28, the major product was **2** (73%). Indene (**33**) was formed in 13% yield. Formation of chrysene (**34**) was also observed (8%), which is likely to be a secondary product of **33**. A small amount of **49** was also formed.



Scheme 28: MFP of 1-Ethynyl-2-Ethylbenzene at 300 °C/50W

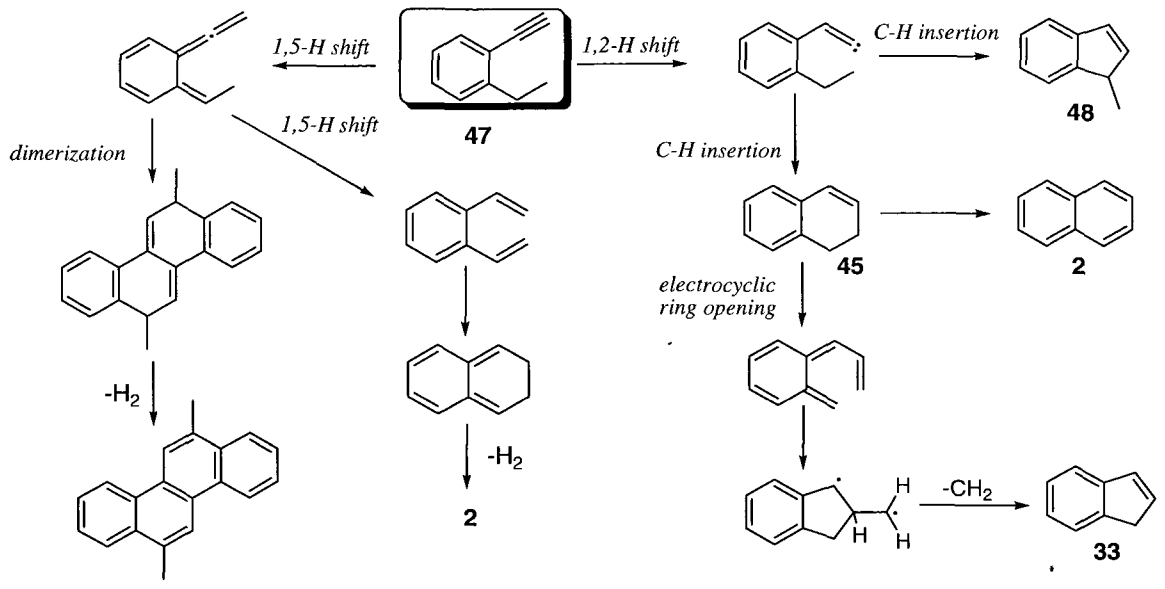
There is no reported literature on thermal rearrangement for the compound under study. Thus, we decided to investigate thermal rearrangement of **47** via FVP and compare the results to MFP. The reaction was carried out in a quartz flow apparatus at 820 °C/0.04 torr. The crude mixture was extracted with dichloromethane and analyzed by ^{1}H NMR.

Components in the mixture were separated by preparative GC and the percent conversion was determined by capillary GC (**Scheme 29**). Each fraction was analyzed by ^{1}H NMR and identified by comparison to known spectra in the literature. The major product was **2** in 35% yield. Methylindene isomers **49** (15%) and **50** (11%) were formed in a higher yield than **48** (2%). Formation of **33** (17%) and **45**(13%) was also observed in the crude mixture.



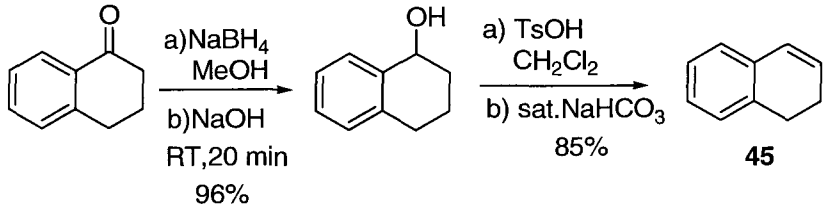
Scheme 29: FVP of 1-Ethynyl-2-Ethylbenzene

MFP and FVP thus gave somewhat different product distribution. Both pyrolysis gave naphthalene (**2**) as the major product. FVP of **47** yields all methylindene isomers and gives higher conversion to **45.** MFP of **47** gives mostly **2** and **33**. Generation of **33** was unexpected but there is a potential route for its formation through **45** (**Scheme 30**). In addition, **34** is formed as a secondary product of **33**. MFP gives a more complex mixture due to the high concentration of reactive intermediates in the reaction zone. Bimolecular processes are more likely to occur with this method. Formation of methylindene isomers was favored by computational studies; the barrier for insertion pathway was lower in energy. It was observed that methylindene isomers are minor products with MFP. Although FVP yields to higher conversion of starting material to methylindene isomers, naphthalene is still the major product.



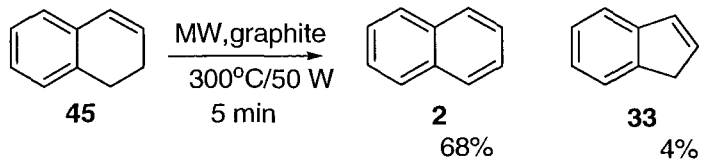
Scheme 30: Proposed Mechanism for Thermal Rearrangement of 1-Ethynyl-2-ethylbenzene

To support the postulated mechanism for formation of indene, we carried out the pyrolysis of **45**. Prior to pyrolysis, **45** was synthesized from α-tetralone[46] (**Scheme 31**).



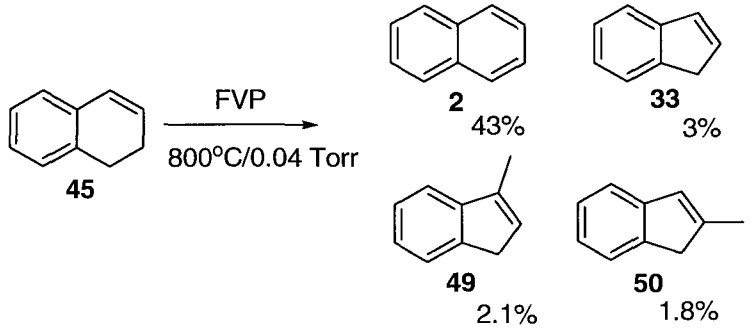
Scheme 31: Synthetic Pathway to 1,2-Dihydronaphthalene

Pyrolysis of **45** was carried out with graphite at 300 °C/50 W for five minutes. The crude product mixture was composed of **2** (68%), **33** (4%) and **45** (22%) as determined by ^{1}H NMR and GC. The percent yield was determined by capillary GC. This confirms a route to indene through **45** (**Scheme 32**).



Scheme 32: Pyrolysis of 1,2-Dihydronaphthalene

FVP of **45** was investigated and results were compared to MFP. The experiment was carried out in a quartz flow apparatus at 800 °C/0.04 torr. The crude mixture was extracted with dichloromethane, concentrated and analyzed by capillary GC and ^{1}H NMR. As indicated by GC analysis, **2** was the major product, formed in 43% yield, and **33** was formed in 4 % yield. In addition, methylindene isomers **49** (2.1%) and **50** (1.8%) were present in the crude mixture (**Scheme 33**). These results further confirm that **33** is a secondary product of **45**.Conversion of **45** to **33** corresponds to loss of :CH_2.



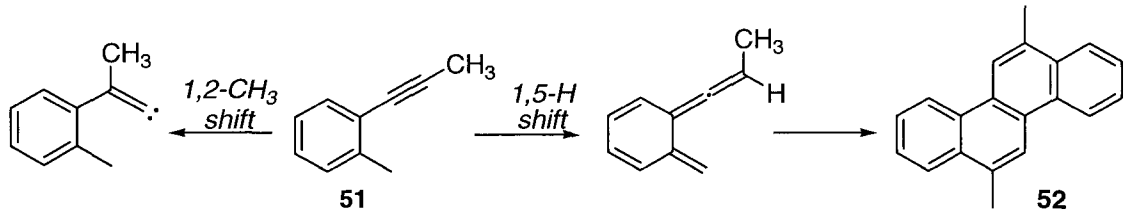
Scheme 33: FVP of 1,2-Dihydronaphthalene

Both MFP and FVP experiments confirm that at high temperature, **45** undergoes dehydrogenation to give **2** as the major product. Formation of **33** from **45** supports the proposed mechanism. FVP of **45** allows for the formation of methylindene isomers **49** and **50**.

Thermal Rearrangement of 1-(2-Methylphenyl)propyne

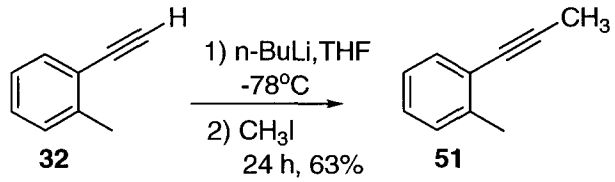
The chemistry of 1-(2-methylphenyl)propyne (**51**) was investigated as an example for tipping a reaction in favor of 1,5-hydrogen shift. According to computational studies

done by Voukides[36], the barrier for a methyl shift is higher in energy relative to a hydrogen shift. Therefore, replacing the alkynyl hydrogen with a methyl group should favor the 1,5-hydrogen shift. This pathway (**Scheme 34**) would allow for synthesis of polycyclic aromatic hydrocarbons (PAH's), more specifically 6,12-dimethylchrysene (**52**).



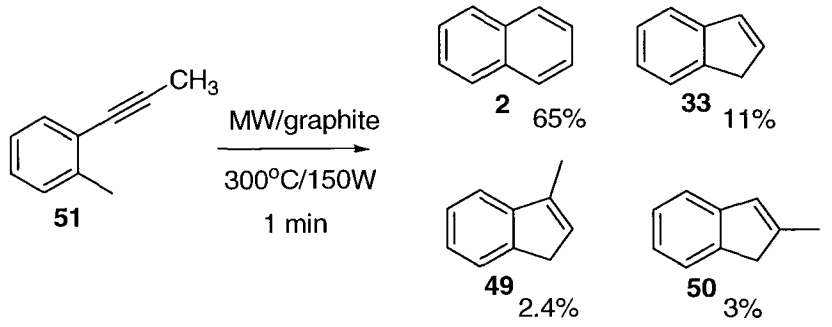
Scheme 34: Proposed Route to 6,12-Dimethylchrysene

Prior to subjecting 1-(2-methylphenyl) propyne (**51**) to MFP and FVP, this material was prepared by alkylation of **32** (**Scheme 35**).



Scheme 35: Synthetic Pathway to 1-(2-Methylphenyl)propyne

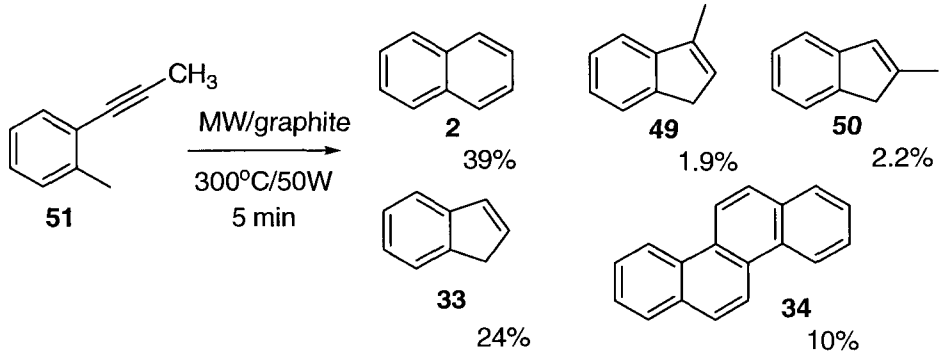
Initial MFP of **51** was carried out with graphite at 300 °C/150 W. The crude mixture was extracted with pentane, followed by dichloromethane extraction. The pentane mixture was filtered, concentrated and analyzed by ^{1}H NMR and capillary GC. The characterization of the components in the mixture was accomplished by the comparison to known spectra.



Scheme 36: Pyrolysis of 1-(2-Methylphenyl) propyne at 300 °C/150 W

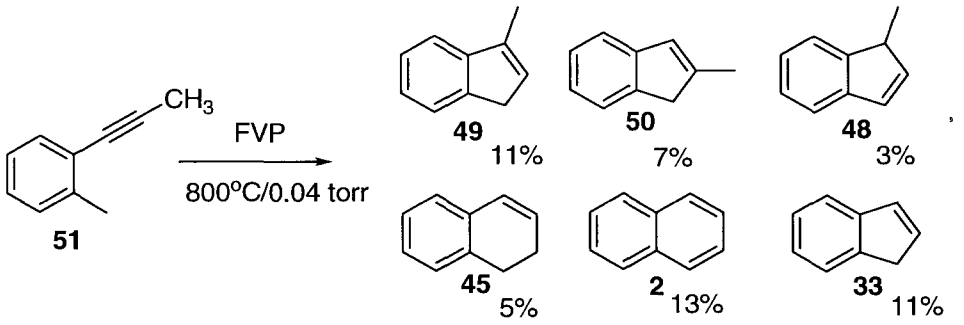
As illustrated in Scheme 36, the major products in the pentane extract were **2** (65 %) and methylindene isomers, **49**(2.4%) and **50**(3%), which were formed in a low yield. Indene (**33**) was observed in the crude mixture in 11% yield.^{1}H NMR analysis of the dichloromethane extract also showed traces of chrysene. Resonances that would indicate formation of **52** were not observed by ^{1}H NMR analysis.

To be consistent with previous results, pyrolysis was repeated using 1:5 ratio of substrate to graphite at 300 °C/50 W for five minutes. The crude mixture was extracted with dichloromethane, filtered, concentrated and analyzed by ^{1}H NMR and capillary GC. As illustrated in Scheme 37, starting material was converted to **2** (39%), **33** (24%), methylindene isomers **49** and **50** (~ 2% each) and **34**(10%).



Scheme 37: Pyrolysis of 1-(2-Methylphenyl) propyne at 300 °C/50 W

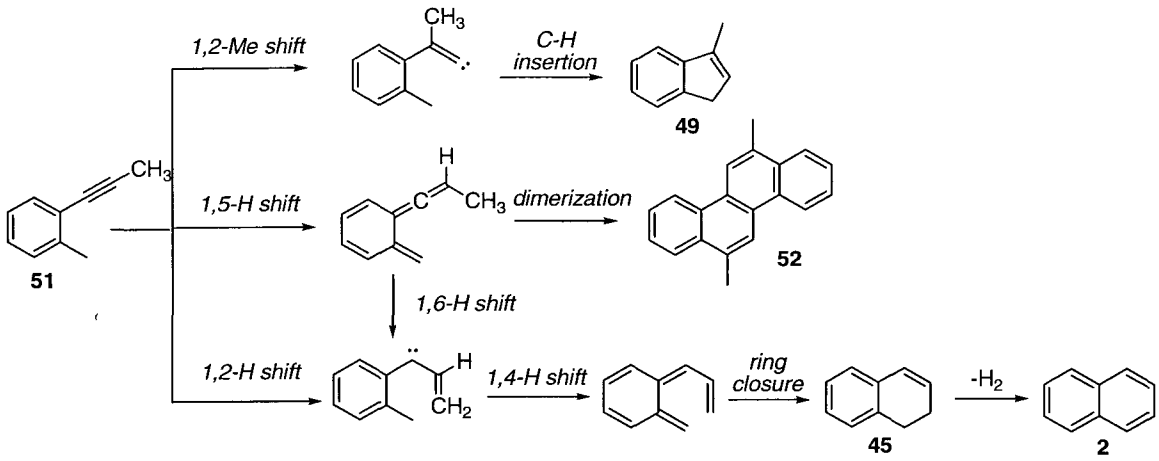
Thermal rearrangements of **51** have not been reported in the literature. To gain a better understanding of this rearrangement, we have investigated FVP of **51**. The pyrolysis was carried out in a quartz flow apparatus at 800 °C/0.05 torr. The crude mixture was analyzed by ^{1}H NMR and capillary GC. Pyrolysis of **51** resulted in **2** as the major product, in addition to smaller amounts of **33** and **49**, both in 11% yield. With FVP, all methylindene isomers are observed by both ^{1}H NMR and capillary GC analysis.



Scheme 38: FVP of 1-(2-Methylphenyl) propyne

As observed with the other rearrangements, MFP favors bimolecular reactions, yielding a somewhat different product distribution as compared to FVP. MFP results indicate that the major product is **2**. Formation of **52**, which would result from 1,5-hydrogen shift and dimerization, was not observed by either ^{1}H NMR or GC analysis. MFP also leads to formation of primary and secondary products. MFP of **51** gives **34** in 10% yield, which is not observed with FVP. Chrysene (**34**) is a secondary product of **33**, which is formed in 24% yield. With MFP, methylindene isomers **49** and **50** were formed in a low yield compared to FVP. FVP of **51** gives a more even distribution of the low molecular weight products and it does not give high molecular weight compounds. ^{1}H NMR spectra from pyrolyses did not show evidence for the formation of **52**. A postulated mechanism for the formation of the products is shown in Scheme 39. We proposed that formation of naphthalene(**2**) results from a vinylidene intermediate that can possibly be

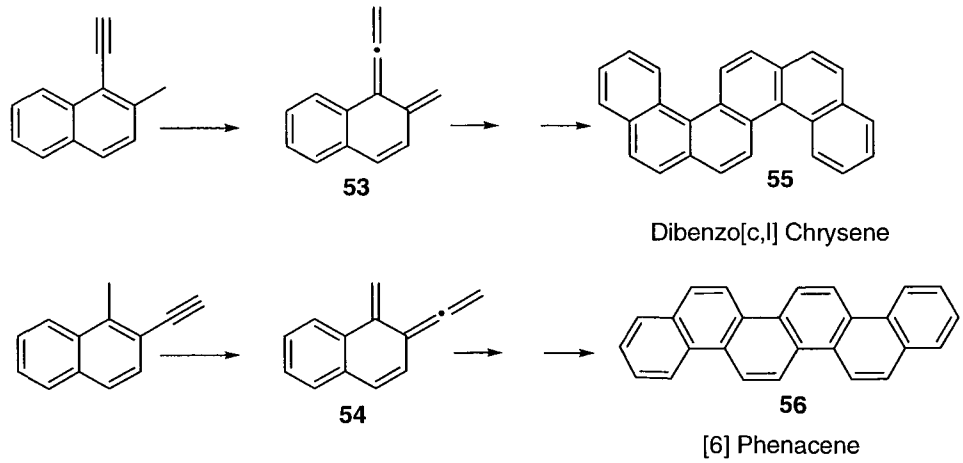
formed through either 1,2-H shift or 1,5-H followed by 1,6-H shift. Computational studies, to determine which pathway would be favored to give **2**, are under investigation.



Scheme 39: Potential Mechanism for Thermal Rearrangement of 1-(2-Methylphenyl) propyne

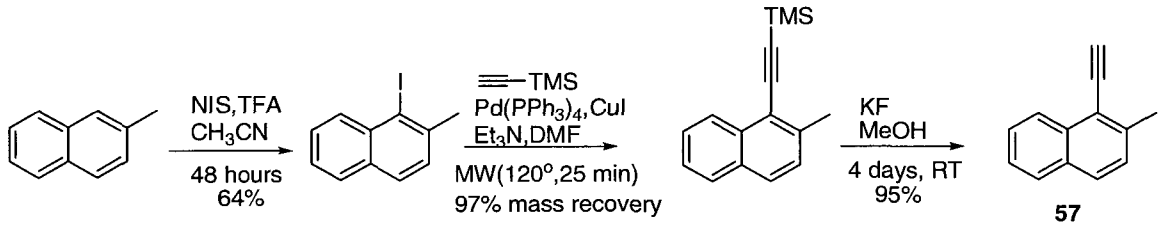
Synthetic Route to Polyacenes

Acenes and phenacenes have been the subject of study for over a century. These polycyclic aromatic hydrocarbons (PAHs) are of current interest in materials science and nanotechnology.[47] Acenes show unique electronic properties due to the topology of their π electron system, and have been studied as promising organic semiconductors.[3] Building on our dimerization route to chrysene, the synthesis of polyacenes was attempted (**Scheme 40**). Based on computational studies[36], 1,5-hydrogen shift may be favored in the naphthalene systems. The proposed synthetic route involves aryl alkyl rearrangements via MFP to afford reactive intermediates **53** and **54**. Each reactive intermediate has the possibility of undergoing dimerization to generate dibenzo[c,l] chrysene (**55**) or [6] phenacene (**56**).

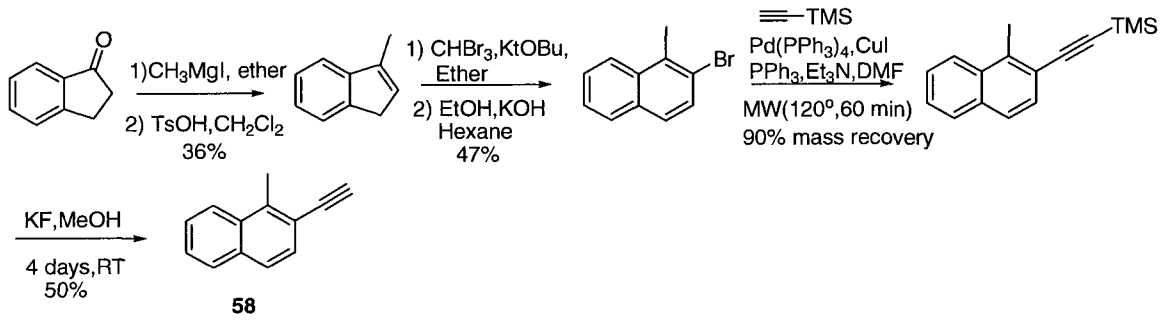


Scheme 40: Synthetic Route to Polyacenes

Before subjecting 1-ethynyl-2-methylnaphthalene (**57**) and 2-ethynyl-1-methylnaphthalene (**58**) to MFP induced cycloaromatization, the starting materials were synthesized via the routes shown in Schemes 41 and 42. Both have been reported previously.[48]



Scheme 41: Synthetic Route to 1-Ethynyl-2-methylnaphthalene



Scheme 42: Synthetic Route to 2-Ethynyl-1-Methylnaphthalene

Sealed tube pyrolysis of **57** was performed with graphite at 300 °C/50 W and a five minute reaction time. The crude mixture was extracted with dichloromethane, filtered, concentrated and subjected to analysis. Interpretation of the crude reaction mixture by ^{1}H NMR analysis was challenging. There were resonances downfield that do not correspond to expected product **55**. This was determined by comparison to spectral data in the literature. [49] We also carried out DFT calculations at the B3LYP/ 6-13G(d) level of theory to predict ^{1}H NMR spectra for both **55** and **56** (**Figure 3**). Calculated ^{1}H NMR resonances for nonplanar **55** agreed well with the reported data (± 2 ppm), but did not match with our experimental ^{1}H NMR spectrum.

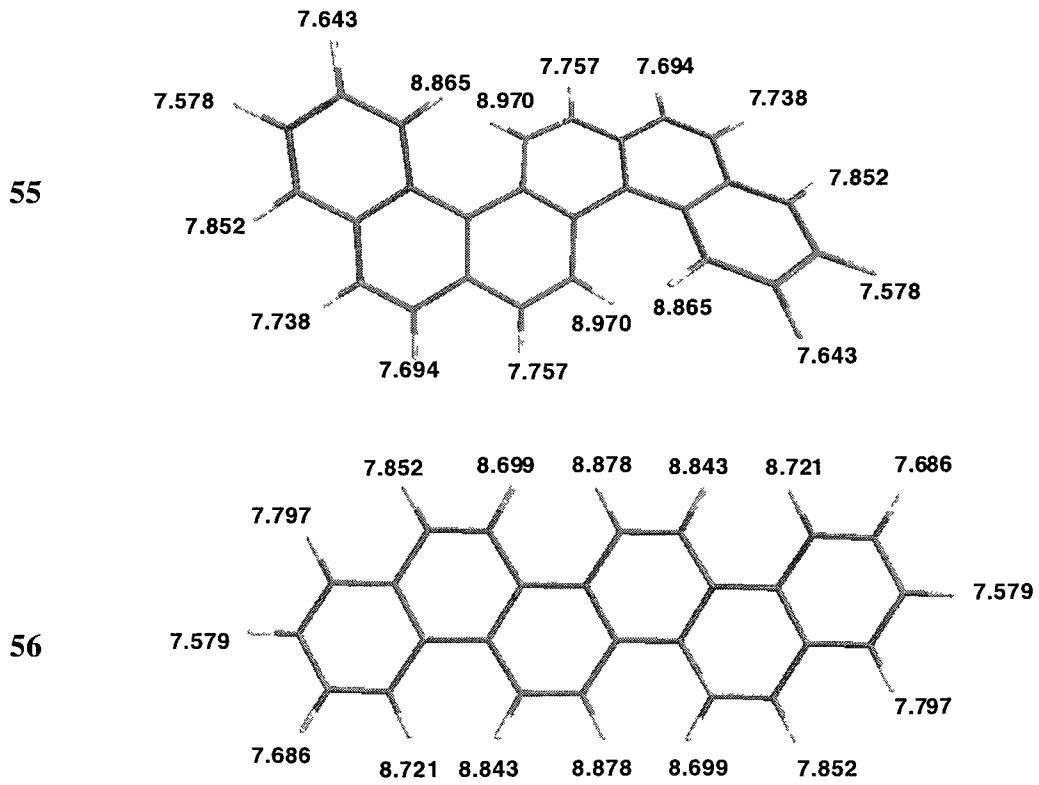
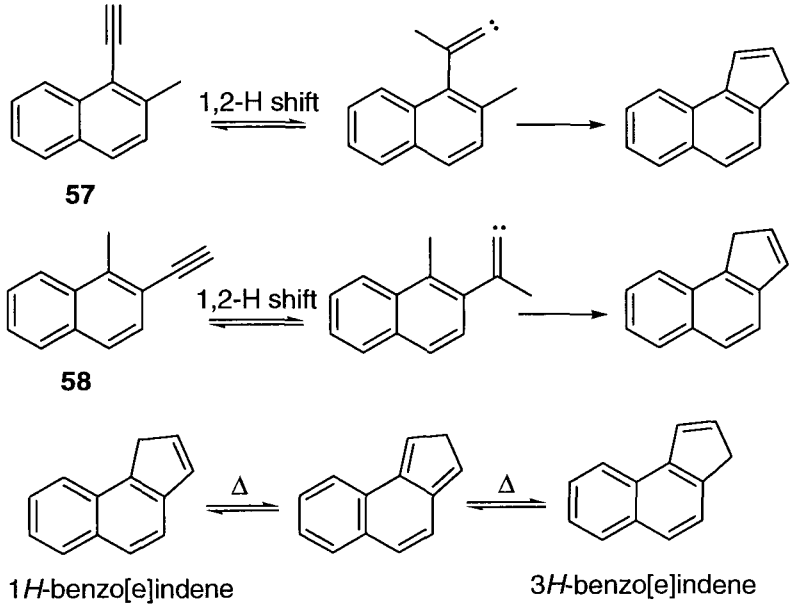


Figure 3: Calculated ^{1}H NMR Resonances for **55** and **56**

Pyrolysis of **58** was carried out under the same conditions. ^{1}H NMR analysis did not support formation of the desired product **56**. Chemical Abstracts and Beilstein were searched to find NMR data on **56**, but no spectral data has been reported. The characterization and identification was solely done by comparison to chemical shifts obtained from DFT calculations.

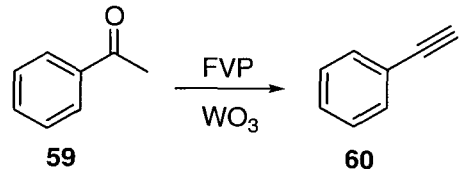
MFP of both **57** and **58** yielded primarily a 1:1 mixture of 1*H*-benzo[e]indene and 3*H*-benzo[e] indene, as determined by ^{1}H NMR analysis of the crude mixture (**Scheme 43**). The characterization of the two products was done by comparison to known spectra.[50] These two compounds are regioisomers and they presumably result from a vinylidene intermediate, followed by C-H insertion. Vinylidene intermediates are formed when **57** and **58** undergo 1,2-hydrogen shift. These two structures should interconvert easily by sequential 1,5-hydrogen shift. Although these results are preliminary, it seems unlikely that this will be a useful route to either **55** or **56**.



Scheme 43: 1*H*-benzo[e]indene and 3*H*-benzo[e]indene

Reactions with New Thermal Sensitizers

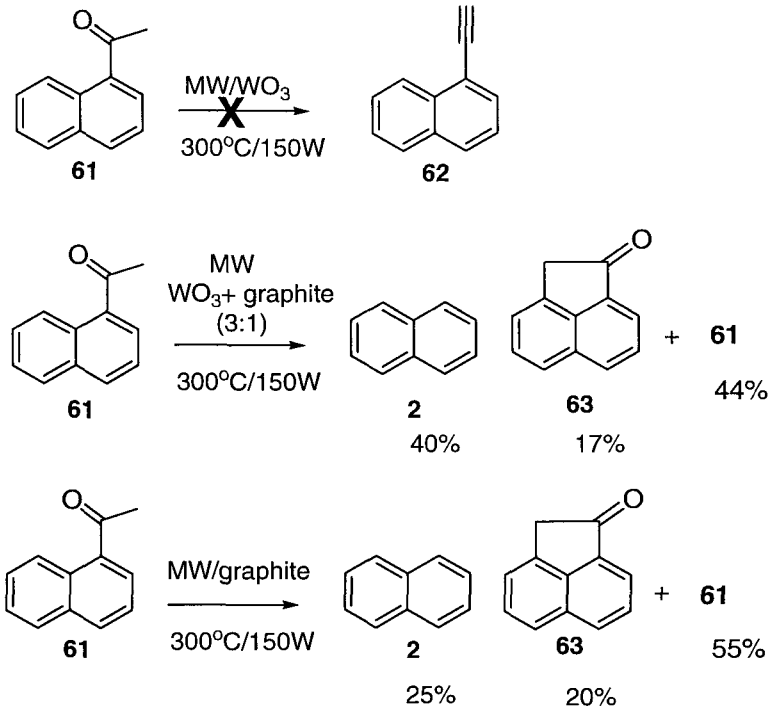
A brief exploration of metal oxides as potential new thermal sensitizers was carried out. Metal oxides are stable at high temperature and often have unique catalytic properties.[8] McNabb and co-workers at the University of Edinburgh have performed FVP with tungsten oxide as a catalyst in the pyrolysis tube. These results (**Scheme 44**) demonstrated deoxygenation of acetophenone (**59**) to generate phenylacetylene (**60**).



Scheme 44: Unpublished Results from McNabb Research Group

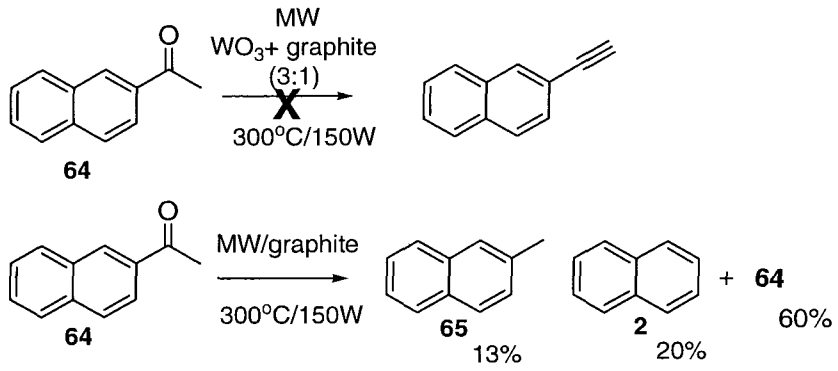
We questioned whether a similar reaction might occur by MFP. Our investigation started by subjecting acetophenone (**59**) to MFP conditions with WO_3. Sealed tube pyrolysis resulted in formation of benzene and residual starting material, as observed by ^1H NMR analysis of the crude mixture. The set temperature (300 °C) was never reached and deoxygenation of **59** to give **60** was not observed. Further investigation (**Scheme 45**) was continued with less volatile 1-acetylnaphthalene (**61**).When **61** was pyrolyzed with WO_3 at 300 °C/150W, the hypothesized product **62** was not seen by ^1H NMR analysis of the crude mixture. Only starting material was observed. During pyrolysis the temperature never reached 300 °C. The same experiment was repeated using a mixture of graphite and WO_3. Pyrolysis of **61** under these conditions resulted in formation of **2** (40%) and 1-acenaphthone (**63**, 17%) identified by comparison to an authentic sample. A third experiment was executed using only graphite as a sensitizer. The crude product mixture

consisted of **2** (25%) and **63** (20%). Thus WO_3 appears to have little effect but graphite sensitized reactions give novel results.



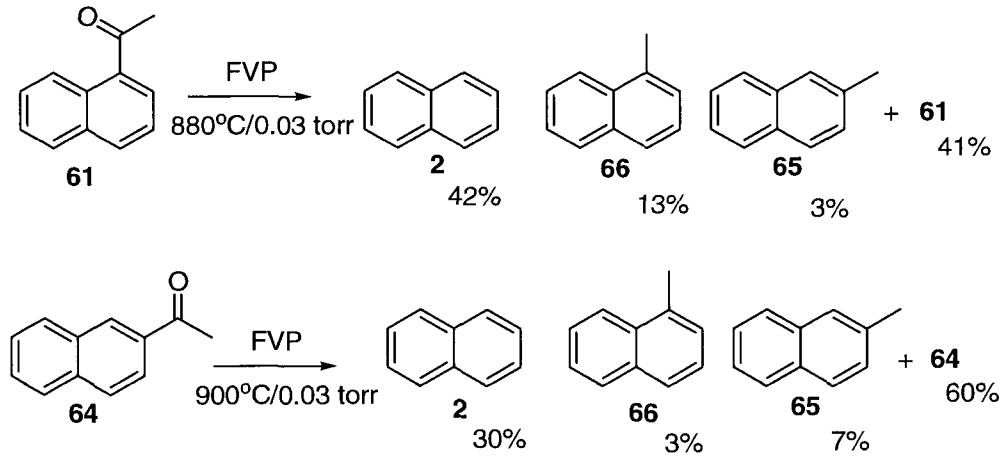
Scheme 45: Pyrolysis of 1-Acetylnaphthalene

The pyrolysis of 2-acetylnaphthalene (**64**) using WO_3 and graphite was next investigated (**Scheme 46**). First, **64** was subjected to pyrolysis with WO_3 and graphite at 300 °C/150W. Only starting material was seen by ^1H NMR analysis. The same experiment was repeated using only graphite as the thermal sensitizer, which resulted in the conversion of starting material to **2** (20%) and 2-methylnaphthalene **65** (13%). Understanding of the mechanism of these reactions is necessary. There is no literature on high temperature reactions involving acetylnaphthalenes. Subjecting acetylnaphthalenes to FVP and comparing results to MFP may elucidate the mechanism.



Scheme 46: Pyrolysis of 2-Acetylnaphthalene

FVP reactions **61** and **64** were carried out at 880-900 °C and 0.03 torr. The crude mixtures were analyzed with capillary GC and ^{1}H NMR. Pyrolysis of **61** at 880 °C /0.03 torr gave a crude mixture composed of **2** (42%), 1-methylnaphthalene (**66**,13%) and **65** (3%). FVP of **64** yielded a low conversion of starting material to the following products: **2** (30%), **65** (7%) and **66** (2 %). The product distribution was determined by capillary GC (**Scheme 47**). ^{1}H NMR analysis of the crude mixture agreed with capillary GC analysis.



Scheme 47: FVP of Acetylnaphthalene Derivatives

We concluded that acetophenone and the isomeric acetylnapthalenes do not undergo deoxygenation upon MFP with or without WO_3. However, other unexpected products,

such as naphthalene and methylnaphthalenes were formed, which demonstrates the potential of MFP for high energy chemistry. Isomerization of methylnaphthalenes was investigated by Cho[13] in our group. It was observed that interconversion between 1-methylnaphthalene and 2-methylnaphthalene can be done by MFP. Both methylnaphthalene isomers also gave naphthalene as one of the products.

CHAPTER III

COMPUTATIONAL STUDIES OF DEHYDRO-DIELS-ALDER REACTIONS

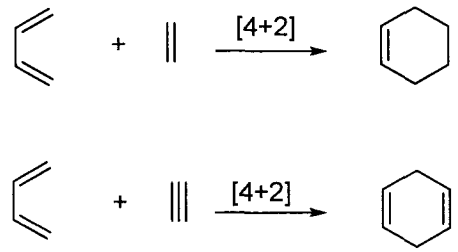
Introduction

Pericyclic reactions have played important roles in organic chemistry as a part of synthetic methodology and for the development of theoretical concepts and computational methods.[51-53] In 1965, Woodward and Hoffman described the principles of orbital symmetry and proposed rules that govern pericyclic reactions.[54-58] Their work entitled "The Conservation of Orbital Symmetry" has had a profound effect on the field of pericyclic reactions.[59] The basic principle of the Woodward/Hoffman rules is that pericyclic reactions are "allowed" when there is an agreement between orbital symmetry of reactants and products. Pericyclic reactions are defined as concerted reactions in which bonds are broken or formed at the same time. In concerted reactions, reactant orbitals transform easily into those of the product, therefore orbital symmetry is conserved. Pericyclic reactions have been widely applied in synthesis, and also occur in biological and biochemical transformations. Pericyclic reactions are classified in five categories: electrocyclic reactions, cycloaddition reactions, sigmatropic reactions, cheletropic reactions, and group transfer reactions.

One subclass of pericyclic reactions referred to as cycloadditions has been widely used reactions in chemistry.[60,61] These reactions have been studied both experimentally

and theoretically. In general, cycloadditions are reactions that result in a ring formation involving two or more unsaturated molecules. This can occur in an intramolecular and intermolecular fashion.

The most well studied type of cycloaddition is the Diels-Alder reaction. These reactions were discovered around 1920 by Otto Diels and Kurt Alder, who were later honored with a Nobel prize.[62] These specific types of pericyclic reactions are [4+2] cycloadditions between a conjugated diene and dienophile, which can be either an alkene or alkyne.[62] Diels-Alder reactions lead to the formation of unstrained products that are generally very stable (**Scheme 48**). Diels-Alder cycloadditions are of synthetic importance because of our ability to predict and control both regioselectivity and stereoselectivity.



Scheme 48: Diels-Alder Reaction

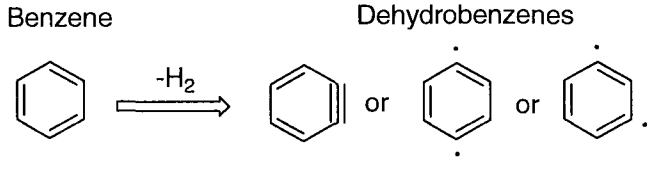
The Woodward/Hoffman rules for cycloadditions are summarized in Table 7. They are used to predict if these reactions can occur thermally or photochemically. These rules can be derived by orbital correlation, frontier molecular orbital theory, or transition state aromaticity analysis.[63] Cycloadditions can proceed in a suprafacial/suprafacial or a suprafacial/antarafacial orientation, although latter are quiet rare.

n=number of electrons	Orientation of Reaction	Thermal	Photochemical
4n	Supra/Supra	Forbidden	Allowed
4n	Supra/Antara	Allowed	Forbidden
4n+2	Supra/Supra	Allowed	Forbidden
4n+2	Supra/Antara	Forbidden	Allowed

Table 7: Woodward/Hoffman Rules for Cycloadditions[63]

The mechanism of the Diels-Alder reaction has been the subject of periodic debate. [64,65]A typical Diels-Alder reaction between a diene and alkene is said to proceed in a concerted process when two new bonds are formed in a single transition state. If formation of the two new σ bonds proceeds simultaneously and at the same rate, the reaction is said to be synchronous concerted. If bonds are formed at different rates, the reaction is considered to be asynchronous concerted. Another possible mechanism is described as stepwise. In this process the first bond is formed to give an intermediate, which then forms a second bond to yield a cycloadduct. The intermediate can possess either zwitterionic or diradical character. [66]

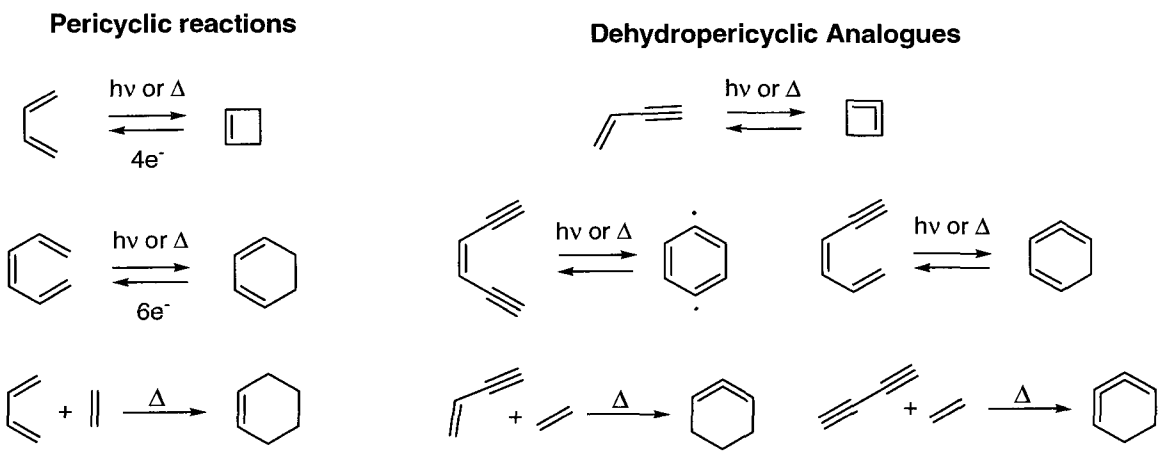
Our group has explored the concept and applications of dehydropericyclic reactions. " Dehydro" structures are those in which hydrogen atoms have been removed. For example, benzene leads to dehydrobenzyne (**Scheme 49**).



Scheme 49: Example of Dehydropericyclic Concept

Dehydropericyclic reactions are conceptually derived from pericyclic reactions by removal of hydrogen atom pairs.[67] The concept of dehydropericyclic reactions offers a new route to reactive intermediates and provides for invention of new chemical reactions. Many examples of dehydropericyclic reactions have been reported in the literature. A recent review by Johnson summarizes illustrative examples from this diverse field.[67]

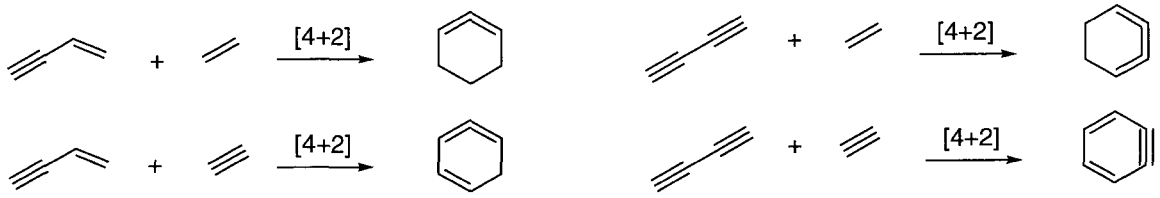
Dehydropericyclic variations on electrocyclic processes, both four and six electron, can be derived by removal of hydrogen atom pairs. Both thermal and photochemical processes are possible, in every case resulting in highly strained products.[68-70] Scheme 50 summarizes some examples of four and six-electron reactions. Examples of these reactions will be explained later in the chapter.



Scheme 50: Four and Six-electron Pericyclic and Dehydropericyclic Reactions

This work focuses on cycloaddition reactions, more specifically Diels-Alder and dehydro Diels-Alder reactions. The scope of these reactions is not limited to dienes. Diene analogues, enynes and diynes, can also undergo [4+2] cycloadditions.[71] These reactions are referred to as dehydro-Diels-Alder reactions due to the loss of two or more hydrogen atoms. Scheme 51 illustrates the four types of dehydro-Diels-Alder reactions. Dehydro-Diels Alder reactions between enyne-ene or enyne-yne moieties afford strained

cyclic allenes. In similar fashion, diyne-ene cycloadditions generate strained cyclic butatrienes, and diyne-yne reactions should generate *ortho*-benzyne intermediates. Dehydro-Diels –Alder reactions thus provide versatile routes to diverse reactive intermediates.



Scheme 51: Dehydro-Diels-Alder Reactions

Our group has previously described a systematic study of intramolecular enyne and diyne cycloadditions. Barriers to reaction for the parent hydrocarbons predicted at the MP4//MP2 level of theory are summarized in Table 8.[67,72,73] These reactions generate strained intermediates, which significantly affects reaction energetics.

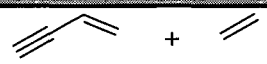
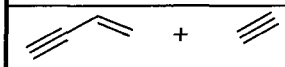
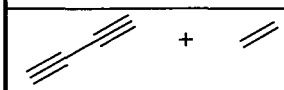
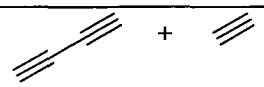
Reaction	$\Delta E_{activation}$ (kcal/mol)	$\Delta E_{reaction}$ (kcal/mol)
	30.8	-12.7
	31.6	-25.4
	35.8	0.63
	35.5	-52.9

Table 8: MP4SDTQ/6-31G(d)//MP2/6-31G(d) Energetics of Dehydro-Diels-Alder Reactions

Project Goals

In this work, computational studies of dehydro-Diels-Alder reactions were conducted at higher levels of theory. The goal was to accurately predict reaction energetics and assess the difference between concerted and stepwise reaction mechanisms. Dehydro-Diels-Alder reactions may be expected to have higher barriers than typical Diels-Alder reactions because strained products are generated. For stepwise enyne-ene and enyne-yne cycloadditions, both regiochemistries were examined.

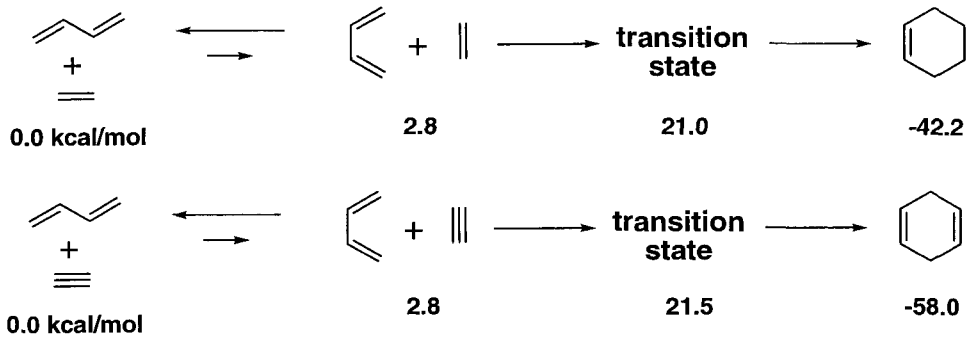
Methodology

Initial 'guess' structures for transition states were built in Spartan 08[74], followed by pre-optimization with constraints at the AM1 level of theory. Geometry optimization of transition states and intermediates was carried out in Gaussian 03[75] at a higher level of theory. The optimization was done using the density functional method at the M05-2X/6-311+G (d,p) level of theory. Optimization was followed by frequency analysis and then single point CCSD (T) calculations with the same basis set. All transition states had one imaginary mode that corresponded to C-C bond formation. For concerted transition states, we were careful to check stability of the wavefunction relative to becoming open shell. Stepwise transition states all had open shell character.

Results and Discussion

The Diels- Alder mechanism has been a subject of much interest and occasional debate.[64,76-92] Numerous computational studies for the mechanism, both concerted and stepwise, have been reported. The results have shown that the energetics of the concerted mechanism are only a few kcal/mol lower than the energetics of stepwise mechanism. Scheme 52 illustrates computed energies for concerted Diels-Alder reaction. According

to our computations, barriers of alkene and alkyne reactions are comparable; the difference is only 0.5 kcal/mol. These agree well with previously reported estimates.[67,72,73]



Scheme 52: CCSD(T)//M05-2X+6-311G(d,p) Energetics for Concerted [4+2] Diels-Alder Reaction

In the sections below, each of the four fundamental dehydro-Diels-Alder reactions is described. In each case, both concerted and stepwise mechanisms are explored (**Figure 4**).

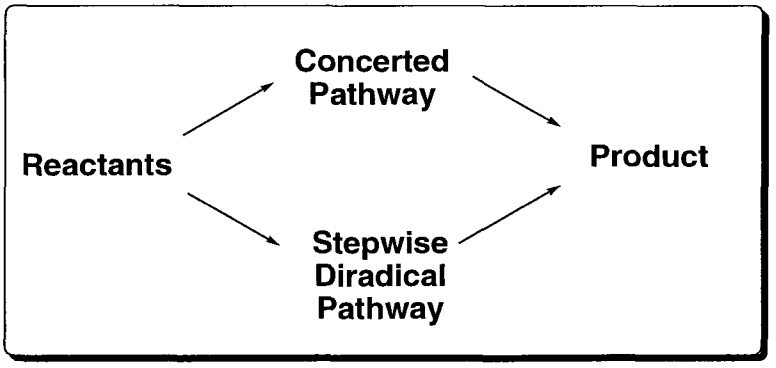
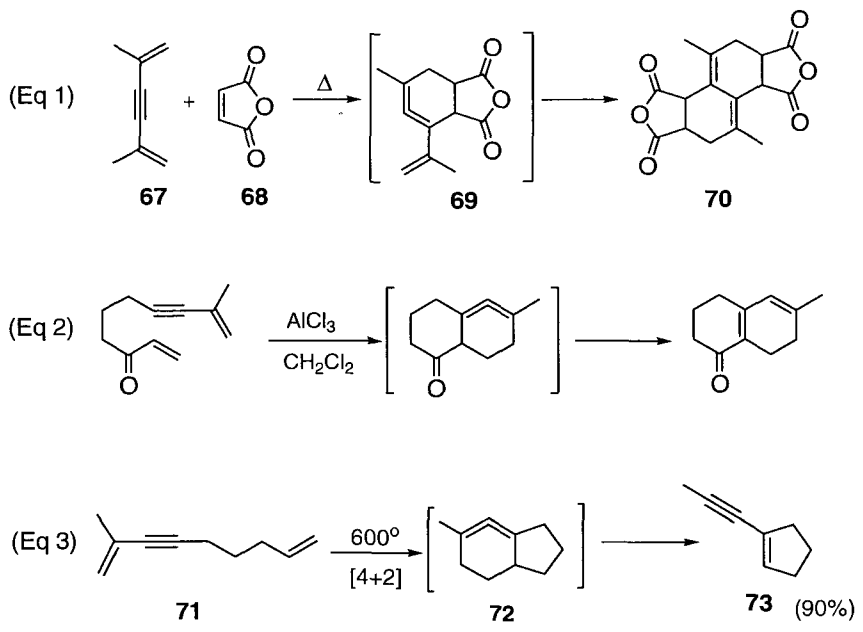


Figure 4: General Approach

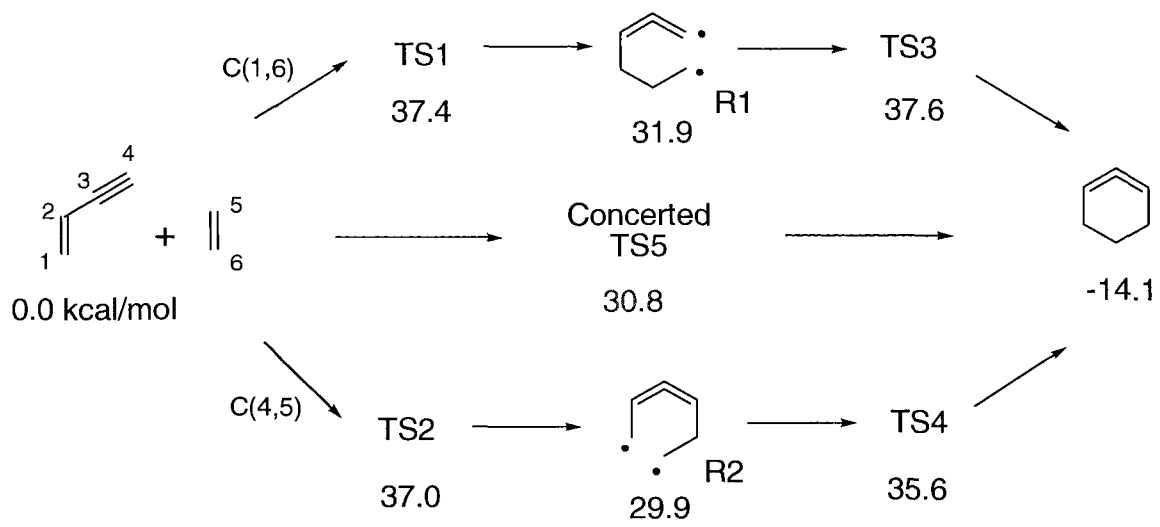
Enyne-Ene Cycloadditions

Enyne-ene cycloadditions (**Scheme 53**) present a convenient route to 1,2-cyclohexadienes. These are reactive intermediates with strain estimated to be 32 kcal/mol.[93] One of the first examples of enyne-ene reaction was reported by Butz and coworkers.[94] They speculated that 1,2-cyclohexadiene intermediate **69** was formed from cycloadditions between **67** and **68**. The intermediate underwent further reaction to yield the observed product **70** (**Eq 1**). Another more recent example of intramolecular enyne-ene cycloadditions was reported by Danheiser and coworkers (**Eq 2**). They have applied enyne-ene cycloadditions to the synthesis of aromatic compounds. The reaction was carried in solution phase in the presence of Lewis acid catalysts.[95] Our research group used flash vacuum pyrolysis to investigate intramolecular enyne-ene cycloadditions.[72] Pyrolysis of **71** resulted in the isolation of **73**. This is believed to arise through formation of cyclic allene intermediate **72**, followed by retro-cycloaddition to form the isolated product (**Eq 3**).



Scheme 53: Reported Enyne-ene Cycloadditions

Scheme 54 summarizes computational results for the parent enyne-ene cycloaddition of vinylacetylene with ethylene. Transition states were located for the concerted reaction and for two stepwise diradical cycloadditions. Addition of the dienophile can occur on both sides of the enyne to give two transition states. The bond formation can occur either between carbon 1 and 6 (**C1,6**) or carbon 4 and 5 (**C4,5**) yielding a diradical intermediate. The diradical intermediate cyclizes, passing through a second transition state, to yield the cyclic allene.

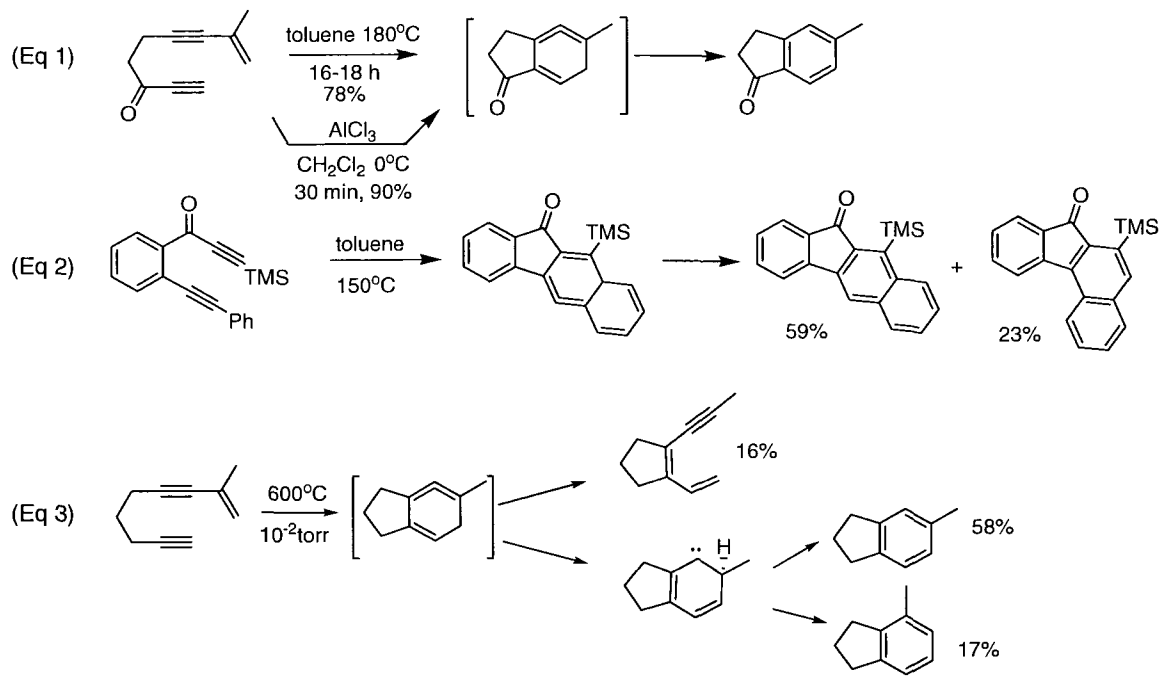


Scheme 54: CCSD(T)6-311+G(d,p)// M05-2X+ 6-311G(d,p)+ ZPVE Computed Energies (kcal/mol) for Enyne-ene Concerted and Stepwise Mechanism

The enyne-ene cycloaddition is only moderately exothermic because of product strain. The concerted barrier of 30.8 kcal/mol is only 9 kcal/mol above the comparable diene reaction and is well below both stepwise transition states. Thus, our computed energies support a concerted cycloaddition. The transition state energies for the stepwise mechanism are ca. 6 kcal/mol higher than the energies for concerted process.

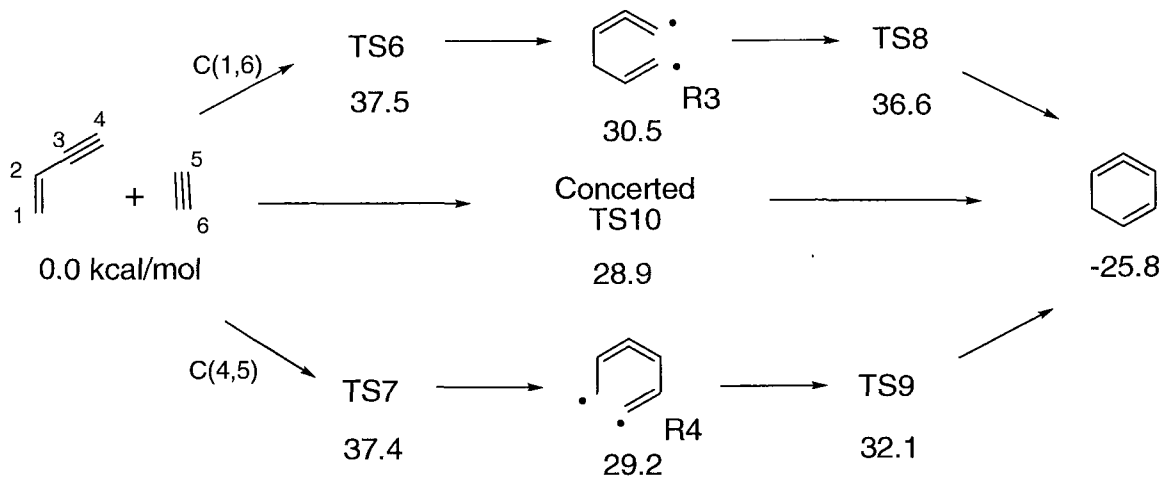
Enyne-Yne Cycloadditions

Enyne-yne cycloadditions will lead to 1,2,4-cyclohexatrienes, another class of strained cyclic allenes. These intermediates have been estimated to have 34 kcal/mol of strain.[93] In most cases, strained cyclic allenes rearrange to aromatic products. Selected examples illustrating enyne-yne cycloadditions are shown in Scheme 55. Examples include intramolecular catalyzed[95] and uncatalyzed[96] reactions (**Eq 1 and Eq 2**) and high temperature reaction (**Eq 3**) performed in our group. [72]



Scheme 55: Intramolecular Enyne-yne Cycloadditions

Earlier computational studies in the Johnson group (**Table 8**), on reaction energetics support the feasibility of cyclic allene intermediates. More detailed energetics on concerted and stepwise mechanisms of this reaction are examined in the present study. Scheme 56 illustrates computational results for enyne-yne cycloaddition. Transition states for concerted and stepwise diradical cycloadditions were located. The stepwise cycloaddition for enyne-yne system occurs through two different pathways generating four different transition states and two diradical intermediates. Bond formation can either occur between carbon 1 and 6 (**C1,6**) or carbon 4 and 5 (**C4,5**) of the enyne-yne moiety. Cyclization of the diradical intermediates affords a strained cyclic allene product.

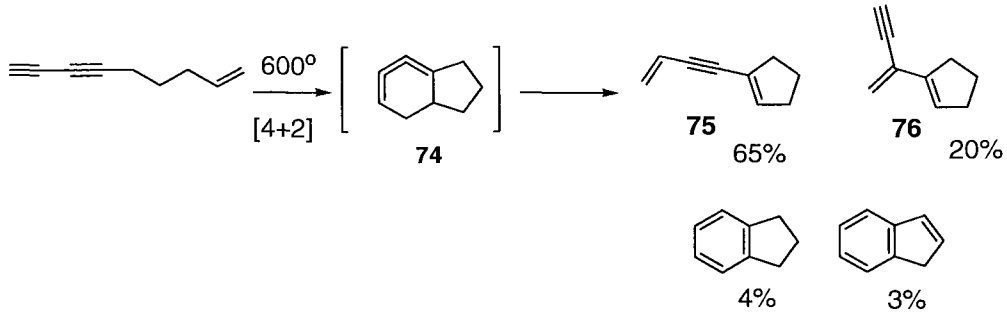


Scheme 56: CCSD(T)6-311+G(d,p)// M05-2X+ 6-311G(d,p)+ ZPVE Computed Energies (kcal/mol) for Enyne-yne Concerted and Stepwise Mechanism

The enyne-yne cycloaddition is exothermic in spite of the strained product formation. The concerted barrier of 32.2 kcal/mol is only 11 kcal/mol above the comparable diene reaction and it lies below both stepwise transition states. This reaction displays very comparable results to the enyne-ene reaction studies, where the transition states of the stepwise mechanism are higher in energy than transition state of the concerted process. The results support a concerted cycloaddition mechanism.

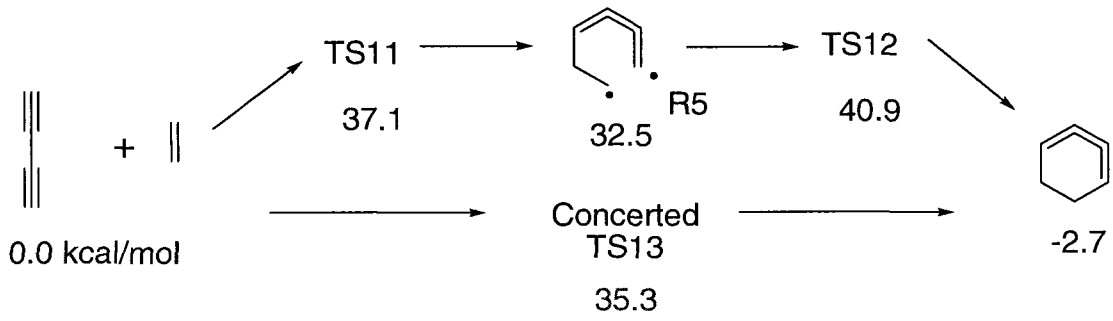
Diyne-ene Cycloadditions

The only example of diyne-ene cycloaddition reaction (**Scheme 57**) was reported by Johnson and coworkers in 1997.[72] Intramolecular cycloadditions under FVP conditions yielded products which supported cycloaddition to give a 1,2,3-cyclohexatriene. This cyclic allene intermediate has been estimated to have 50 kcal/mol of strain.[93] The results show that the diyne-ene moiety undergoes cycloadditions to give cyclic butatriene intermediate **74** which subsequently goes through ring opening to give major product **75** in 65% yield. Formation of **76** in 20% yield was speculated to result from a stepwise process.



Scheme 57: Cyclic Butatriene Synthesis in Johnson Group

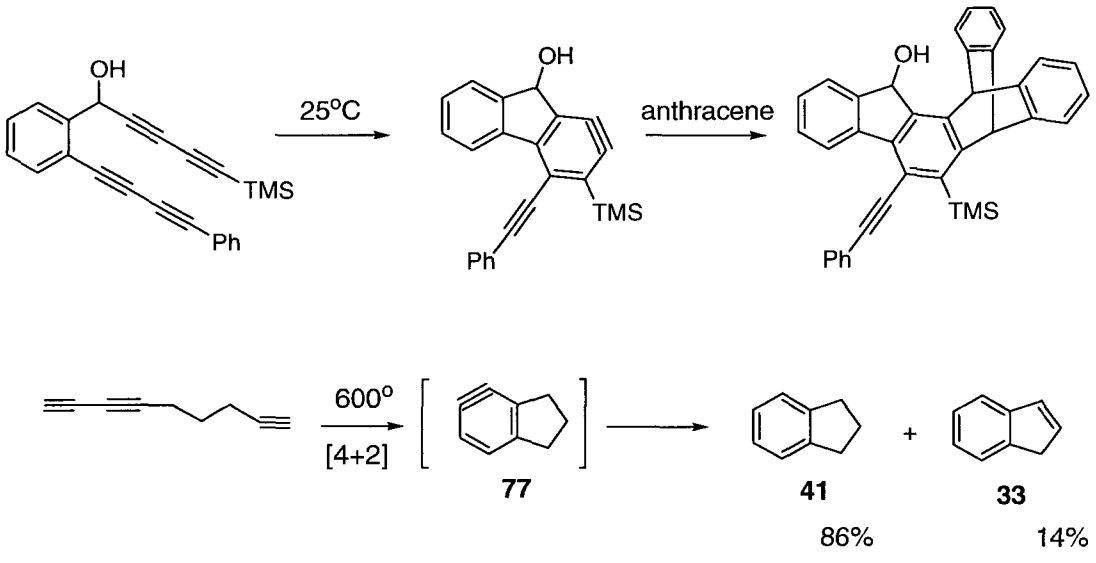
Earlier MP4//MP2 computational studies in our group (**Table 8**) predicted an increase in the activation barrier of 5 kcal/mol compared to a diene reaction. Building on the previous work, we carried out calculations to predict reaction barriers for concerted and stepwise cycloaddition pathways. Results for cycloaddition of butadiyne and ethylene are summarized in Scheme 58. Transition states were located for the concerted and stepwise diradical pathways. Diyne-ene cycloaddition reaction is only slightly exothermic consistent with the formation of a strained 1,2,3-cyclohexatriene. The energies of stepwise and concerted transition states are very similar, but the concerted transition state is slightly favored relative to the stepwise transition state. By comparison to enyne reactions, the stepwise transition states are all similar. In this case, the concerted reaction barrier rises significantly.



Scheme 58: CCSD (T)6-311+G(d,p)// M05-2X+ 6-311G(d,p)+ ZPVE Computed Energies (kcal/mol) for Diyne-ene Concerted and Stepwise Mechanism

Diyne-yne cycloaddition

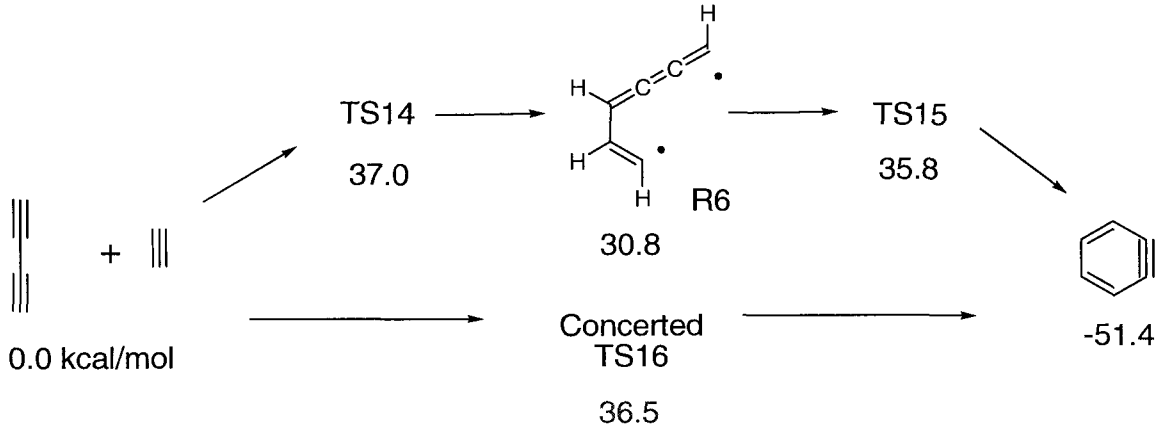
Diyne-yne [4+2] cycloadditions can potentially proceed through stepwise or concerted mechanisms to give *ortho*-benzyne. This reaction is expected to be highly exothermic in spite of the product strain energy. Selected examples of reported diyne-yne cycloadditions are shown in Scheme 59. Intramolecular diyne-yne reaction to give benzyne intermediate was reported by Ueda who also reported a number of similar cycloadditions.[97,98] This reaction proceeds at room temperature, presumably through a stepwise mechanism. The example of diyne-yne cycloaddition was observed in our group, by Bradley and Johnson, at high temperature. Flash vacuum pyrolysis of 1,3,8-nonatriyne yielded aromatic products **41** and **33**, which are believed to arise from benzyne intermediate **77**.[73]



Scheme 59: Intramolecular Diyne-yne Cycloadditions

Earlier work done in our group used MP4//MP2 theory (**Table 8**) to predict a concerted mechanism and favorable reaction energies. It was estimated that cycloaddition of butadiyne and acetylene has an activation energy of 35.5 kcal/mol.[99]In the present,

work we performed computational studies on concerted and stepwise mechanisms of diyne-yne cycloaddition using higher level theory.



Scheme 60: CCSD(T) 6-311+G(d,p)// M05-2X+ 6-311G(d,p)+ ZPVE Computed Energies (kcal/mol) for Diyne- yne Concerted and Stepwise Mechanism

Scheme 60 summarizes our predicted energetics for diyne-yne cycloaddition. Transition states were located for concerted and stepwise diradical cycloaddition pathways. These results show that the concerted and stepwise reactions have nearly identical barriers. The addition of acetylene to 1,3-butadiyne in a stepwise process gives a diradical intermediate with a barrier of 37 kcal/mol. This is only 0.5 kcal/mol higher relative to the transition state for the concerted process (36.5 kcal/mol).

Conclusions

CCSD (T)//M05-2X computations have been carried out for both concerted and stepwise processes in the four types of dehydro-Diels-Alder reactions. All four reactions are exothermic in spite of high product strain energy. For enyne-ene and enyne-yne cycloadditions, addition to both ends of the enyne was considered. Based on computed energies for the stepwise mechanisms, the enyne-ene and enyne-yne reaction are more likely to undergo a concerted process to yield cyclic allenes. The concerted transition states for these two reactions are ca. 6-7 kcal/mol lower in energy than the stepwise

transition states (**Scheme 54** and **56**). For the diyne-ene reaction, energies of the transition state for the stepwise mechanism are very close in energy to the transition state of the concerted process. This reaction will presumably occur through a concerted mechanism to yield 1, 2, 3-cyclohexatriene. However, the concerted transition state is only 0.5 kcal/mol lower in energy compared to the stepwise transition state for the diyne-yne reaction. Diyne-ene and diyne-yne reactions can proceed through a concerted mechanism to give strained products, however the computed energy differences between the concerted and the stepwise transition states are very small. We note that in every case, the CCSD(T)//DFT energeics for concerted reactions are within 3 kcal/mol of earlier MP4//MP2 predictions (**Table 8**). Further studies of the free energies for these reactions at high temperature should give a better understanding of the mechanism.

CHAPTER IV

EXPERIMENTAL SECTION

General Experimental

Instrumentation

^{1}H NMR Spectra were recorded on a Varian Mercury 400 MHz NMR spectrometer. All spectra were measured with deuterochloroform ($CDCl_3$) as a solvent and tetramethylsilane ($(CH_3)_4Si$) as an internal standard, unless otherwise noted. $CDCl_3$ was purchased from Cambridge Isotope Laboratory and stored over molecular sieves. Chemical shifts are reported in parts per million (ppm) relative to the internal standard.

^{13}C NMR Spectra were recorded on a Varian Mercury 400 MHz NMR spectrometer. All spectra were measured with deuterochloroform ($CDCl_3$) as a solvent and tetramethylsilane ($(CH_3)_4Si$) as an internal standard, unless otherwise noted. $CDCl_3$ was purchased from Cambridge Isotope Laboratory and stored over molecular sieves. Chemical shifts are reported in parts per million (ppm) relative to the internal standard.

Analytical Gas Chromatography (GC) was performed with a Hewlett-Packard HP 6890 instrument equipped with a flame ionization detector connected to a Hewlett-Packard HP 3395 integrator.

A J&W scientific DB-5 capillary column (30 m x 0.32mm) was used for analytical separations.

Preparative Gas Chromatography (GC) was performed with a Gow-Mac instrument equipped with a thermal conductivity detector connected to a Linear chart recorder. A 15% Carbowax 20 M on Chromosorb W-HP 80/100 mesh (10' x ¼' stainless steel) column was used at specified temperatures. Method parameters were as follows: Column 130 °C, injector 210 °C and detector 245 °C, unless otherwise specified.

Molecular Modeling calculations were performed using Spartan'08[74]and Gaussian '03.

Solvents and Reagents

Solvents: Diethyl ether, dichloromethane (CH_2Cl_2), benzene and methanol were purchased from EMD or Pharmco-AAPER and used without further purification. Pentane was purchased from Alfa Aesar and used without further purification. Tetrahydrofuran and hexanes were purchased from EMD or Pharmco-AAPER and distilled prior to use.

Reagents: All reagents were of sufficient quality and used as obtained from the following companies: Fisher Scientific (Acros), Alfa Aesar, Aldrich, Lancester, and Cambridge Isotope Laboratories.

Chromatography and Adsorbents

Thin Layer Chromatography (TLC) was completed using Whatman polyester plates coated with 250 μm layer silica gel doped with phosphor. Visualization was done with an ultraviolet light at 254 nm.

Silica Gel: 220-440 mesh Alfa Aesar silica gel 60 was used as obtained from the company.

Alumina: 50-200 micron Acros activated neutral aluminum oxide was used as obtained from the company.

General Procedure: Microwave Flash Pyrolysis

All experiments were conducted in a CEM Discover microwave reactor using the closed vessel method. Substrates were mixed with graphite, silicon carbide or metal oxides by light grinding. Pyrolyses were carried out in 5 mL capped Pyrex tubes lined with a smaller quartz tube (12 x 70 mm; glassblower fabrication) and purged with nitrogen. The experiments were carried out with two different power modes (dynamic and fixed) as provided by the instrument.

Dynamic power control applies a specified amount of maximum power, defined by the user, to reach the control point. The instrument modulates this set power automatically, based on sensor feedback data, to ensure the control point is reached rapidly, but with limited error (temperature or pressure) "overshooting". The parameters used with this power control included: 300 °C maximum temperature and 150 W maximum power. Irradiation was generally conducted with a five minute ramp time and one minute hold time, followed with two minute cooling periods.

Fixed power control allows the user to apply the desired power from the beginning of the reaction without a ramping time. This option applies a specified amount of energy for a specified amount of time. Maximum temperature and pressure limits modify instrument operation, either by ending the irradiation cycle or by adjusting the power, if either is reached. The fixed power control option can be programmed in two options, control and safe. We utilized the control fixed power option. With this option, the instrument applies programmed power until the temperature setpoint is reached, then

switches to a feedback loop, which modulates the amount of power applied to maintain the setpoint temperature. The parameters used with this power control included: 300 °C maximum temperature and 50 W maximum power. Irradiation was generally conducted with five minutes hold time followed by a two minute cooling period.

The products were isolated by rinsing the tube and graphite with pentane and dichloromethane and filtering the extracts through neutral alumina. Samples were concentrated and analyzed directly by 400 MHz NMR, TLC or GC. Unless otherwise stated, quoted percentages represent product ratios not absolute yields.

Microwave Flash Pyrolysis Safety

Caution! Graphite, carbon nanotubes and silicon carbide heat rapidly in a microwave field, generating high surface temperatures and occasional sparks. To minimize explosion hazards, thermally sensitized experiments should be conducted in quartz glassware under nitrogen. An external explosion shield is recommended for open vessel experiments. For closed-vessel experiments, the pressure should be monitored closely; tubes may hold residual pressure after cooling.[9]

General Procedure: Flash Vacuum Pyrolysis Experiments

Flash vacuum pyrolysis experiments (FVP) were performed using a Lindberg model 55035 thermolysis oven containing a 50 cm quartz tube. One end of the tube was fitted with a 50 mL round bottom flask containing the sample. The opposite end of the column was equipped with a dry ice trap, which was connected to a Welch dual-stage vacuum pump. The sample was cooled using dry ice. The pyrolysis apparatus was evacuated and maintained at 10^{-2} torr pressure while the sample was warmed and evaporated. The sample moved through pyrolysis oven (hot zone), which was held at a

constant temperature, before condensing in the cold trap. Experiments were performed in the 750-900 °C range. At the end of pyrolysis, the system was flushed with nitrogen to facilitate product isolation.

Chapter I Experimental

Pyrolysis of Azulene on Graphite

Azulene (**1**, 20 mg, 0.16 mmol) and graphite (50 mg; Aldrich synthetic graphite, 20 microns) were mixed using a mortar and pestle and transferred to a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. Product was isolated by washing the cooled tube with small volumes of $CDCl_3$ and filtering through neutral alumina. Analysis by 400 MHz ^1H NMR showed the mixture to be 35% azulene (**1**) and 65% naphthalene (**2**).

Pyrolysis of Azulene on Silicon Carbide

Azulene (**1**, 20 mg, 0.16 mmol) and silicon carbide (50 mg; Alfa Aesar, 2 micron powder, alpha-phase) were ground lightly together and transferred to a quartz tube (12 x 70 mm). Reaction was run "closed vessel" as above at 300 °C/150 W for a two minutes hold time. Blue solid had sublimed into the upper part of the tube. ^1H NMR analysis of the product showed 84% azulene (**1**) and 16% naphthalene (**2**).

Pyrolysis of Phthalic Anhydride on Graphite

Phthalic anhydride (**3,** 29 mg, 0.19 mmol) and graphite (102 mg Aldrich synthetic graphite, 20 microns) were mixed using a mortar and pestle and transferred to a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. Product was isolated by washing the cooled tube with small volumes of dichloromethane and filtering through neutral alumina to yield brown solid in 33% mass recovery. Product analysis by ^{1}H NMR showed the following composition: benzene (**8**, 51%), biphenyl (**4**, 24 %), naphthalene (**2**, 10 %), biphenylene (**5**, 5 %), triphenylene (**7**, 6%), and anthracene (**9**, 6%)

Pyrolysis of Phthalic Anhydride on Silicon Carbide

Phthalic anhydride (**3**, 27 mg, 0.18 mmol) and silicon carbide (100 mg) were mixed using a mortar and pestle and pyrolyzed as above at 300 °C/150 W for five minutes ramp time and one minute hold time. Products were isolated by washing the quartz tube with small volumes of $CDCl_3$ and filtering through neutral alumina directly into an NMR tube. Analysis by ^{1}H NMR showed the following composition: phthalic anhydride (**3**, 26%), benzene (**8**, 45%), biphenyl (**4**, 21%), naphthalene (**2**, 7 %), biphenylene (**5**, 1.2 %), triphenylene (**7**, 0.5%).

Pyrolysis of Benzobarrelene (**11**)

Benzobarrelene (**11**, 27 mg, 0.18 mmol) and graphite (66 mg; Aldrich synthetic graphite, 20 microns) were mixed using a mortar and pestle and transferred to a quartz tube (12 x

70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300°C/150 W for five minutes ramp time and one minute hold time. Product was isolated by washing the cooled tube with small volumes of $CDCl_3$ and filtering through neutral alumina. Analysis by 400 MHz ^1H NMR showed the mixture to be 41% benzobarrelene (**11**) and 59% naphthalene (**2**). Characterization was accomplished by comparison to ^{1}HNMR of authentic samples.

Pyrolysis of Dibenzobarrelene

Dibenzobarrelene (2 mg, 0.01 mmol) and graphite (13 mg; Aldrich synthetic graphite, 20 microns) were mixed using a mortar and pestle and transferred to a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. Product was isolated by washing the cooled tube with small volumes of $CDCl_3$ and filtering through neutral alumina. Analysis by 400 MHz ^1H NMR showed the mixture to be 45% dibenzobarrelene and 55% anthracene (**9**). Characterization was accomplished by comparison to ^{1}HNMR of authentic samples.

Pyrolysis of *ortho*-Terphenyl on Graphite

ortho-Terphenyl (**12**, 23 mg, 0.01 mmol) and graphite (80 mg Aldrich synthetic graphite, 20 microns) were mixed using a mortar and pestle and transferred to a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was

inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. Products were isolated by washing the tube with small volumes of $CDCl_3$ and filtering through neutral alumina directly into an NMR tube. ^1H NMR analysis showed the mixture to be composed of starting material (38%), triphenylene (**7**, 11 %), biphenyl (**4**, 17%) and benzene (**8**, 34%).

Pyrolysis of *ortho*-Terphenyl on Tungsten Oxide (WO_3)

ortho-Terphenyl (**12**, 30.2 mg, 0.13 mmol) and tungsten oxide (100 mg) were mixed using a mortar and pestle and pyrolyzed as above at 300 °C/150 W five minutes ramp and one minute hold time. Products were isolated by washing the tube with small volumes of $CDCl_3$ and filtering through neutral alumina directly into an NMR tube. ^1H NMR analysis showed the mixture to be composed of starting material (66%), triphenylene (**7**, 14 %), biphenyl (**4**, 7%) and benzene (**8**, 13%).

Pyrolysis of *ortho*-Terphenyl on Copper (II) Oxide

ortho-Terphenyl (**12**, 45 mg, 0.20 mmol) and copper(II) oxide (180 mg) were mixed using a mortar and pestle and pyrolyzed as above at 300 °C/150 W for five minutes ramp time and one minute hold time. Products were isolated by washing the tube with small volumes of $CDCl_3$ and filtering through neutral alumina directly into an NMR tube. ^1H NMR analysis showed the mixture to be composed of starting material (95%), triphenylene (**7**, 1.4%), biphenyl (**4**, 1.9%) and benzene (**8**, 1.9%).

Pyrolysis of 1, 1'-Binaphthyl on Graphite

1,1'- Binaphthyl (**13**, 25 mg, 0.10 mmol) and graphite (100 mg; Aldrich synthetic graphite, 20 microns) were mixed using a mortar and pestle and transferred to a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300 °C/100 W for five minutes ramp time and one minute hold time. Product was isolated by washing the cooled tube with small volumes of $CDCl_3$ and filtering through neutral alumina. Product analysis by ^1H NMR showed the following: 1, 1'-binaphthyl (**13**, 66%), perylene (**14**, 5%), naphthalene (**2**, 28 %), benzo[j]-fluoranthene (**15**, 0.6%). Characterization was accomplished by comparison to ^1H NMR of authentic samples.[100]

Pyrolysis of Benzhydrol on Graphite

Benzhydrol (**18**, 65 mg, 0.40mmol) and graphite (120 mg; Aldrich synthetic graphite, 20 microns) were mixed using a mortar and pestle and transferred to a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite layer. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using fixed power mode at 300 °C/50 W for five minutes. The crude product mixture was extracted with dichloromethane, filtered through neutral alumina, concentrated and analyzed by ^1H NMR and capillary GC. Capillary GC analysis showed the mixture to be 35% benzhydrol (**18**), 2% fluorene (**17**), 65% diphenylmethane (**19**), and 28% benzophenone (**20**). Characterization was done by comparison to known ^1H NMR spectra of authentic samples.

Synthesis of Diphenylmethylacetate (**21**)

The procedure of Sajiki *et al.* was modified.[101] A 25 mL round-bottomed flask, equipped with magnetic stir bar and septum, was charged with benzhydrol (1.1 g, 6mmol) dissolved in pyridine (2mL) under a nitrogen atmosphere. Acetic anhydride (1.2 g, 12mmol) was added to the flask and the reaction was stirred for 48 hours. The reaction was quenched with water (100 mL) and ether (100 mL). Combined organic layers were washed with 1M HCl (10 mL), water (100 mL), brine (30mL), dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure. The crude mixture was purified by column chromatography with hexanes to afford pure diphenylmethylacetate as a cloudy liquid (1.2 g, 85%).Characterization was done by ^{1}H NMR and ^{13}C NMR and compared to known spectra in the literature. [102,103]

Pyrolysis of Diphenylmethylacetate on Graphite

Diphenylmethylacetate (**21**, 26 mg, 0.12mmol) and graphite (85 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using fixed power mode at 300 °C/50 W for five minutes. The crude product mixture was extracted with dichloromethane, filtered through neutral alumina, concentrated and analyzed by ^{1}H NMR and capillary GC. Capillary GC analysis showed the mixture to be 15% starting material, 8% fluorene (**17**), and 62% diphenylmethane (**19**). Characterization was done by comparison to known ^{1}H NMR spectra of authentic samples.

Synthesis of 1-Benzyl-2-bromobenzene (**22**)

The procedure of Odedra *et al.* was modified.[30] A 35 mL microwave vial, equipped with magnetic stir bar and septum, was charged with 2-bromobenzyl alcohol (1.87g, 10.0 mmol) and benzene (20 mL) under a nitrogen atmosphere. Iron (III) chloride (160 mg, 10% mol) was added and vial was flushed with nitrogen. The reaction was run in the CEM microwave reactor, closed vessel, at 150 °C/300W for 30 minutes. The crude reaction mixture was filtered through silica plug via vacuum filtration, washed with diethyl ether (~50mL), and concentrated. The crude reaction mixture was washed with hexanes to remove remaining iron (III) chloride, filtered and concentrated under reduced pressure. Column chromatography over silica gel, eluting with hexanes, afforded pure 1-benzyl-2-bromobenzene as a colorless liquid (1.1g, 50%). ^{1}H NMR and ^{13}C NMR compared to literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.16 (dd, J = 12.4, 6.0 Hz, 4H), 7.10 – 7.04 (m, 1H), 7.02 – 6.97 (m, 1H), 4.08 (s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 140.73, 139.82, 133.21, 131.45, 129.37, 128.85, 128.25, 127.82, 126.63, 125.28, 42.11.

Pyrolysis of 1-Benzyl-2-bromobenzene (300 °C/300 W)

1-Benzyl-2-bromobenzene (**22**, 73 mg, 0.30 mmol) and graphite (86 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite layer. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300°C/300 W for five minutes ramp time and one minute hold time. Crude product mixture was extracted with dichloromethane, filtered through neutral alumina, and concentrated to

brown oil in 48% (35.3 mg) mass recovery. The crude mixture was analyzed by ^{1}H NMR and capillary GC. Capillary GC analysis showed the mixture to be 23% fluorene (**17**), 4% diphenylmethane (**19**), and 73% starting material. Characterization was done by comparison to known ^{1}H NMR spectra of authentic samples.

Pyrolysis of 1-Benzyl-2-bromobenzene (300 °C/50 W)

1-Benzyl-2-bromobenzene (**22**, 63 mg, 0.25 mmol) and graphite (89 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using fixed power mode at 300 °C/50 W for five minutes. The crude product mixture was extracted with dichloromethane, filtered through neutral alumina, concentrated to brown oil in 80% (50 mg) mass recovery. The crude mixture was analyzed by ^{1}H NMR and capillary GC. Capillary GC analysis showed the mixture to be 37% fluorene (**17**), and 7% diphenylmethane (**19**), and 50% starting material. Characterization is done by comparison to known ^{1}H NMR spectra of authentic samples.

Flash Vacuum Pyrolysis of 1-Benzyl-2-bromobenzene

1-Benzyl-2-bromobenzene (**22**, 132mg, 0.53 mmol) was passed during 30 minutes through a horizontal quartz tube maintained at 800 °C evacuated to pressure of 0.03 torr. The product mixture condensed in a trap cooled with dry ice. At the end of the reaction, the vial was flushed with nitrogen and product mixture was extracted with dichloromethane. Solvent was removed under reduced pressure to yield yellow oil in 83% mass recovery. Capillary GC analysis showed the mixture to be composed of

starting material (90%) and fluorene (10%). Characterization is done by comparison to known ^{1}H NMR spectra of authentic samples.

Chapter II Experimental

1-Trimethylsylil (ethynyl) biphenyl

A 50 mL round-bottomed flask, equipped with a septum and magnetic stir bar, was charged with 2-bromobiphenyl (1.0 g, 4.3 mmol) and (trimethylsilyl) acetylene (1.8 g, 18.3 mmol). Dimethylformamide (10 mL) and diethylamine (5 mL) were added to the flask via syringe under nitrogen atmosphere. The round-bottomed flask was purged with nitrogen under the vacuum (0.5 torr). Dichlorobis(triphenylphosphine) palladium(II) (190 mg, 0.3 mmol) and copper iodide (48.6mg, 0.3 mmol) were added to the mixture in the flask and purged with nitrogen. The reaction was run at 60 °C for 24 hours. The crude mixture was poured over 0.1M HCl (20-25 mL) and extracted with diethyl ether (3x15 mL). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (2x15-20 mL) and water (2x 15-20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure to afford 1-trimethylsylil (ethynyl) biphenyl in 90% mass recovery. The product formation was checked by ^{1}H NMR analysis and compared to literature.

2-Ethynylbiphenyl (**28**)

A 25 mL round-bottomed flask, equipped with septum and magnetic stir bar, was charged with 1-trimethylsylil (ethynyl)biphenyl (628 mg, 2.5 mmol), anhydrous potassium fluoride (690g, 5.0 mmol) and methanol (6 mL). The flask was purged with nitrogen. The reaction was stirred at room temperature for 24 hours under nitrogen atmosphere. The reaction was monitored by TLC. The crude mixture was diluted with water (15 mL) to

dissolve the remaining potassium fluoride, and then extracted with diethyl ether (3x 20 mL). Combined ether layers were washed with water (20 mL), dried over $MgSO_4$ and filtered. Column chromatography eluting with hexanes afforded pure 2-ethynylbiphhenyl as yellow oil (280 mg, 45 %). ^{1}H NMR data agreed with the literature.[104]

Pyrolysis of 2-Ethynylbiphenyl on Graphite

2-Ethynylbiphenyl (**28**, 23 mg, 0.13 mmol) and graphite (68.0 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Reaction was run "closed vessel" in a CEM Discover reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. Product was isolated by washing the cooled tube with small volumes of $CDCl_3$ and filtering through neutral alumina. ^{1}H NMR analysis showed ca. 90 % conversion to products, with formation of phenanthrene (**29**, 94 %) and anthracene (**9**, 6%), as well as traces (<1%) of benz[a]azulene (**30**).

Pyrolysis of 2-Ethynyltoluene on Graphite

2-Ethynyltoluene (**32**, 220 mg, 1.9mmol) and graphite (413 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Pyrolysis was carried out in a CEM reactor using fixed power mode at 300 °C/50W for five minutes. After cooling, the crude product mixture was extracted with pentane followed by extraction with dichloromethane. Both extracts were concentrated and analyzed separately by GC and ^{1}H

NMR. The components in the pentane extract were analyzed and separated by preparative GC with the following parameters: column (122 °C), injector (204 °C), and detector (220 °C). Each component in the crude mixture was trapped in a tube vial cooled in dry ice/acetone, and analyzed by ^{1}HNMR and analytical GC. The crude pentane mixture was composed of the following components in order of elution: o-xylene (**38**,14%), 2-ethyltoluene (**39**,11%), 2-vinyl toluene (**40**,7%), indan (**41**,10%), and indene (**33**,34%). Percentages are determined by cutting and weighing peaks on the chromatogram. The crude dichloromethane extract was composed primarily of chrysene (**34**) and its isomers benz[a]anthracene (**42**) and benzo[c] phenanthrenes (**43**) as determined by ^{1}H NMR analysis. The compounds were identified by comparing to known spectra in the literature.[41,42]

Pyrolysis of 2-Ethynyltoluene on Graphite (variable concentration)

Each sample was prepared by mixing graphite (50 mg; Aldrich synthetic graphite, 20 microns) with the substrate in a small quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. The pyrolysis was run in a CEM microwave reactor using dynamic power mode at 300 °C/150W for five minutes ramp time and one minute hold time. After cooling, the crude product mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated. The crude mixture was analyzed by ^{1}H NMR and capillary GC and identified by comparison to authentic samples. Percent conversion of each component in the crude mixture was determined by capillary GC (**Table 9**).

mass (substrate)	mass (graphite)	2-Vinyltoluene (40)	Indan (41)	Indene (33)	Naphthalene (2)
10 mg	**50 mg**	x[a]	x[a]	68	8
20 mg	**50 mg**	4	5	64	4
30 mg	**50 mg**	7	6	40	x[b]

a) not detected, b) % of the product < 1 Note: The numbers indicate the % of isolated product

Table 9: Pyrolysis of 2-Ethynyltoluene at Variable Concentration

Pyrolysis of 2-Ethynyltoluene on Graphite (variable reaction times)

2-Ethynyltoluene (**32**, 30 mg, 0.26 mmol) and graphite (50 mg Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. The pyrolysis was run in a CEM microwave reactor using fixed power mode at 300 °C/50W for 1, 2, 3.5 or 5 minutes. After cooling, the crude product mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated. The crude mixture was analyzed by ^{1}H NMR and capillary GC and identified by comparison to authentic samples. Percent conversion of each component in the crude mixture was determined by capillary GC. The % mass recovery was 40-50% in all cases.

Time (minutes)	2-Vinyltoluene (40)	Indan (41)	Indene (33)	Naphthalene (2)	Chrysene (34)
1	x[a]	2	53	5	10
2	2	2	49	4	11
3.5	2	2	44	3	8
5	2	3	53	4	12

a) not detected; Note: The numbers indicate the % of isolated product

Table 10: Pyrolysis of 2-Ethynyltoluene at Variable Reaction Times

Flash Vacuum Pyrolysis of 2-Ethynyltoluene

2-Ethynyltoluene (**32**, 360mg, 3.0 mmol) was passed during 30 minutes through a horizontal quartz tube maintained at 750 °C evacuated to pressure of 0.02 torr. The

product mixture condensed in a trap cooled with dry ice. At the end of the reaction, the vial was flushed with nitrogen and product mixture was extracted with dichloromethane. Solvent was removed under reduced pressure to yield yellow oil in 51% mass recovery. ^{1}H NMR analysis showed the mixture to be composed of starting material and indene in 5:1 ratio.

Pyrolysis of 1-ethynyl-2-ethylbenzene on Graphite (300°C/150W)

1-Ethynyl-2-ethylbenzene (**47**, 30 mg, 0.23 mmol) and graphite (150 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite layer. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Pyrolysis was carried out in a CEM reactor using dynamic power mode at 300 °C/ 150W for five minutes ramp and one minute hold time. After cooling, the crude mixture was first extracted with pentane and then dichloromethane. Two extracts, pentane and dichloromethane, of the crude mixture were analyzed by ^{1}H NMR and capillary GC. Capillary GC analysis showed pentane extract to be composed of: naphthalene (**2**, 63%), indene (**33**, 11%) and 3-methylindene (**49**, 4%).

Pyrolysis of 1-Ethynyl-2-ethylbenzene on Graphite (300 °C/50W)

1-Ethynyl-2-ethylbenzene (**47**, 32 mg, 0.25 mmol) and graphite (151 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite layer. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Pyrolysis was carried out in a CEM reactor using fixed power mode at 300 °C/ 50W for five minutes. After cooling, the crude mixture was extracted with dichloromethane, filtered through neutral

alumina and concentrated to dark orange oil in 59% mass recovery. The crude mixture was analyzed by ^{1}H NMR and capillary GC. Capillary GC analysis showed the crude mixture to be composed of naphthalene (**2**, 73%), indene (**33**, 13%) and 3-methylindene (**49**, 2%), 1,2-dehydronapthalene (**45**, 2%) and chrysene (**34**, 8%).

Flash Vacuum Pyrolysis of 1-Ethynyl-2-ethylbenzene

1-Ethynyl-2-ethylbenzene (**47**,116 mg, 0.89 mmol) was passed through a horizontal quartz tube maintained at 820 °C evacuated to pressure of 0.04 torr over 30 minutes. The product mixture condensed in a trap cooled with dry ice. At the end of the reaction, the vial was flushed with nitrogen and the crude mixture was extracted with dichloromethane. Solvent was removed under reduced pressure to yield dark yellow oil in 74% (87 mg) mass recovery. Components in the crude mixture were separated by preparative GC, analyzed by ^{1}H NMR and capillary GC and identified by comparison to authentic samples. Capillary GC analysis gave the percent of each component in the mixture: indene (**33**,17%), 1,2-dihydronaphthalene (**45**,13%), naphthalene (**2**, 35%), 3-methylindene (**49**,15%), 2-methylindene (**50**,11%), 1-methylindene (**48**,2%).

Pyrolysis of 1-(2-Methylphenyl)propyne (300 °C/150W)

1-(2-Methylphenyl)propyne (**51**,130 mg, 1.0 mmol) and graphite (200 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite layer. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen and sealed. Pyrolysis was carried out in a CEM reactor using dynamic power mode at 300 °C/ 150W for one minute hold time. The crude mixture was first extracted with pentane, followed by the extraction with dichloromethane. Both extracts were filtered through neutral alumina and concentrated.

The pentane extract was recovered as yellow oil in 15 % mass recovery. The pentane extract was analyzed by ^{1}H NMR and capillary GC to obtain the percent of each component in the mixture. Identification was done by comparison to spectral data of authentic samples. Capillary GC of pentane extract showed following product distribution: indene (**33**, 11 %), 3-methylindene (**49**, 2.4%), 2-methylindene (**50**, 3%), and naphthalene (**2**, 65%). The dichloromethane extract was recovered as brown solid in 20% mass recovery. The components in the dichloromethane extract were separated by preparative TLC with hexane as an eluent. The separation yielded four different bands which were analyzed by ^{1}H NMR analysis. The nonpolar band contained naphthalene (**2**). Other bands yielded mixtures of chrysene (**34**) and traces of benz[a] anthracene (**42**) and benzo[c] phenathrene (**43**).

Pyrolysis of 1-(2-Methylphenyl)propyne (300 °C/50W)

1-(2-Methylphenyl)propyne (**51**,35 mg, 0.27 mmol) and graphite (150 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the graphite layer. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Pyrolysis was carried out in a CEM reactor using fixed power mode at 300°C/ 50W for five minutes. After cooling, the crude mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated to dark orange oil in 59% mass recovery. The crude mixture was analyzed by ^{1}H NMR and capillary GC. Capillary GC analysis showed crude mixture to be composed of naphthalene (**2**, 39%), indene (**33**, 24%) and 3-methylindene (**49**, 1.9%), 2-methylindene (**50**, 2.2%), and chrysene (**34**, 10%).

Flash Vacuum Pyrolysis of 1-(2-Methylphenyl)propyne

1-(2-Methylphenyl)propyne (**51**,130 mg, 1.0 mmol) was passed through a horizontal quartz tube maintained at 800°C evacuated to pressure of 0.05 torr for 20 minutes. The product mixture condensed in a trap cooled with dry ice. At the end of the reaction, the vial was flushed with nitrogen and the crude mixture was extracted with dichloromethane. Solvent was removed under reduced pressure to yield dark yellow oil in 95% mass recovery. Components in the crude mixture were separated by preparative GC, analyzed by ^{1}H NMR and indentified by comparison to authentic samples. Capillary GC analysis gave the percent of each component in the mixture: indene (**33**,11%), 3-methylindene(**49**,11%), 2-methylindene(**50**,7%),1-methylindene(**48**,3%), 1,2-dihydronaphthalene (**45**,5%) and naphthalene (**2**,13%).

Pyrolysis of 1,2-Dihydronaphthalene on Graphite

1,2-Dihydronaphthalene (**45**, 89 mg, 0.68 mmol) and graphite (85 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm).A small plug of glass wool was placed above graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Pyrolysis was carried out in a CEM reactor using fixed power mode at 300 °C/ 50W for five minutes. The crude mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated to yellow oil. Capillary GC analysis indicated following conversion to products: naphthalene (**2**, 69%) and indene (**33**, 4%).^{1}H NMR analysis agreed with GC data.

Flash Vacuum Pyrolysis of 1,2-Dihydronaphthalene

1,2-Dihydronaphthalene (**45**,150 mg, 1.2 mmol) was passed through a horizontal quartz tube maintained at 800 °C evacuated to pressure of 0.04 torr over 30 minutes. The

product mixture condensed in a trap cooled with dry ice. At the end of the reaction, the vial was flushed with nitrogen and crude mixture was extracted with dichloromethane. Solvent was removed under reduced pressure. The crude mixture was analyzed by ^{1}H NMR and capillary GC and identified by comparison to authentic samples. Percent conversion of each component in the crude mixture was determined by capillary GC: naphthalene (**2**, 43%), indene (**33**, 4%), 3-methylindene (**49**, 2.1%), and 2-methylindene (**50**, 1.8%).

Pyrolysis of Indene on Graphite

Indene (**33**, 54 mg, 0.46 mmol) and graphite (250 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Pyrolysis was carried out in a CEM reactor using fixed power mode at 300 °C/50 W for five minutes. The crude mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated to yield dark orange solid in 46 % mass recovery. Capillary GC analysis showed following product distribution: indene (**33**, 60%), naphthalene (**2**, 3%), and chrysene (**34**, 31%).

Pyrolysis of Indene on Graphite (variable reaction times)

Indene (**33**,30 mg, 0.26 mmol) and graphite(150 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm).A small plug of glass wool was placed above the graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen and sealed. The pyrolysis was run in a CEM microwave reactor using fixed power mode at 300 °C/50W for 1, 2, 3.5 or 5 minutes. After cooling, the crude product mixture was extracted with dichloromethane, filtered through neutral

alumina and concentrated. The crude mixture was analyzed by ^{1}H NMR and capillary GC and identified by comparison to authentic samples. Percent conversion of each component in the crude mixture was determined by capillary GC.

Time (minutes)	Indan (41)	Indene (33)	Naphthalene (2)	Chrysene (34)
1	2	83	1	12
2	3	82	2	13
3.5	3	76	2	19
5	3	71	3	22

Note: The numbers indicate the % of isolated product

Table 11: Pyrolysis of Indene at Variable Reaction Times

Pyrolysis of Indan

Indan (**41**, 30 mg, 0.25 mmol) and graphite (153 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen and sealed. Pyrolysis was carried out in a CEM reactor using fixed power mode at 300 °C/50 W for five minutes. The crude mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated to yield brown solid in 86 % mass recovery. Capillary GC analysis showed following product distribution: indene (**33**, 48%), naphthalene (**2**, 4%), chrysene (**34**, 8%), and starting material (30%).

1-Trimethysylil (ethynyl)-2-ethylbenzene

The procedure of Erdélyi and Gogoll was modified.[37]A 35 mL microwave vial, equipped with a septum and magnetic stir bar, was charged with 1-ethyl-2-iodobenzene (5.0 g, 21.5mmol) and (trimethylsilyl) acetylene (3.3 g, 33.4 mmol). Dimethylformamide (5 mL) and triethylamine (9 mL) were added to the vial via syringe under nitrogen atmosphere. The vial was purged with nitrogen under the vacuum (0.5 torr). Tetrakis(triphenylphosphine)palladium(0) (459 mg, 0.4 mmol) and copper iodide (184

mg, 0.9 mmol) were added to the mixture in the vial and purged with nitrogen. The reaction was run in a microwave reactor at 120 °C/50W for 25 minutes. The crude mixture was poured over 0.1M HCl (20-25 mL) and extracted with diethyl ether (3x15 mL). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (2x15-20 mL) and water (2x 15-20 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure to afford 1-trimethylsylil (ethynyl)-2-ethylbenzene in 99% mass recovery. The product formation was checked by ^1H NMR analysis and compared to literarture.[48]

1-Ethynyl-2-Ethylbenzene (**47**)

A 25 mL round-bottomed flask, equipped with septum and magnetic stir bar, was charged with 1-trimethylsylil (ethynyl)-2-ethylbenzene (4.70 g, 23.3 mmol), anhydrous potassium fluoride (1.41 g, 24.1 mmol) and methanol (15 mL). The flask was purged with nitrogen. The reaction was stirred at room temperature five days under nitrogen atmosphere. The reaction was monitored by TLC. The crude mixture was diluted with water (15 mL) to dissolve the remaining potassium fluoride, and then extracted with diethyl ether (3x 20 mL). Combined ether layers were washed with water (20 mL), dried over $MgSO_4$ and filtered. Column chromatography eluting with hexanes afforded pure 1-ethynyl-2-ethylbenzene as dark orange oil (979 mg, 32 %). ^1H NMR (400 MHz,$CDCl_3$) δ: 7.45 (d, 1H, J=7.6Hz) 7.26 (t, 1H, J=7.5Hz), 7.19 (d, 1H, J=7.7Hz), 7.12 (t, 1H, J=7.5Hz), 3.22 (s, 1H), 2.81 (q, 2H, J=7.6Hz), 1.23 (t, 3H, J=7.6Hz);^{13}C NMR (400 MHz,$CDCl_3$) δ:147.1, 133.1, 129.2, 128.2, 125.8, 121.5, 82.6, 80.7, 27.8, 15.1. ^1H and ^{13}C NMR data agreed with the literature.[48]

1-Iodo-2-methylnaphthalene

The procedure of Castanet *et.al* was modified.[105] A 250 mL round-bottomed flask was charged with 2-methylnaphthalene (5.00g, 35.2 mmol) dissolved in anhydrous acetonitrile (90 mL). N-iodosuccinimide (8.70 g, 38.7 mmol) was added and the color of the mixture turned orange. The reaction was stirred under nitrogen atmosphere. Trifluoroacetic acid (2 mL) was added dropwise to the reaction mixture via syringe. The reaction was refluxed for 48 hours under nitrogen atmosphere. The color of the reaction mixture went from orange to dark brown overtime. The crude mixture was diluted with water (40 mL) and extracted with diethyl ether (3 x 25 mL). Combined organic layers were washed with aqueous $NaHSO_3$ (2x 25mL), water (25 mL), dried over $MgSO_4$, filtered and concentrated. Simple distillation of the crude mixture afforded pure 1-iodo-2-methylnaphthalene as a brown oil (3g, 64%).^{1}H NMR (400 MHz,$CDCl_3$) δ: 8.19 (d, 1H, J=8.6Hz), 7.67 (m, 2H, J=8.2Hz, J=17.9Hz), 7.50 (t, 1H), 7.40 (t, 1H, J=7.4Hz), 7.29 (d, 1H, J=8.3Hz), 2.65 (s, 3H). NMR data agreed with known spectra in the literature.[106]

1-Trimethylsylil (ethynyl)-2-methylnaphthalene

The procedure of Erdélyi and Gogoll was modified.[37]A 35 mL microwave vial, equipped with a septum and magnetic stir bar, was charged with 1-iodo-2-methylnaphthalene (3.0 g, 11.2 mmol) and (trimethylsilyl) acetylene (2 g, 20.4 mmol). Dimethylformamide (5 mL) and triethylamine (10 mL) were added to the vial via syringe under nitrogen atmosphere. The vial was purged with nitrogen under the vacuum (0.5 torr). Tetrakis(triphenylphosphine)palladium(0) (258mg, 0.23 mmol) and copper iodide (85 mg,0.44 mmol) were added to the mixture in the vial and purged with nitrogen. The reaction was run in the CEM microwave reactor, closed vessel, at 120 °C/50W for 25

minutes. The crude mixture was poured over 0.1M HCl (20-25 mL) and extracted with diethyl ether (3x15 mL). The combined organic layers were washed with saturated solution of $NaHCO_3$ (2x15-20 mL), water (2x15-20 mL), dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure to afford 1-trimethylsylil (ethynyl)-2-methylnaphthalene in 97% mass recovery.

1-Ethynyl-2-Methylnaphthalene (**54**)

A 25 mL round-bottomed flask, equipped with a septum and magnetic stir bar, was charged with 1-trimethylsylil (ethynyl)-2-methylnaphthalene (3 g, 12.6 mmol), anhydrous potassium fluoride (730 mg, 12.6 mmol) and methanol (15 mL). The reaction was stirred at room temperature four days under nitrogen atmosphere. The crude mixture was diluted with water to dissolve remaining potassium fluoride and extracted with diethyl ether (3x 20 mL). Combined ether layers were washed with water (20 mL), dried over $MgSO_4$, filtered and concentrated. Column chromatography eluting with hexanes afforded pure 1-ethynyl-2-methylnaphthalene as orange oil (674 mg, 95 %).^{1}H NMR (400 MHz,$CDCl_3$) δ: 8.26 (d, 1H, J=8.4Hz), 7.68 (d, 1H, J=8.2Hz), 7.62 (d, 1H, J=8.4Hz), 7.45 (t, 1H, J=7.6Hz), 7.34 (t, 1H, J=7.5Hz), 7.22 (d, 1H, J=8.4Hz), 3.60 (s, 1H), 2.56 (s, 3H).

1-Methylindan-1-ol

The procedure of Charette and Lebel was modified.[107]A 250 mL, three-necked round-bottomed flask containing magnesium turnings (3.23 g, 120 mmol) was equipped with glass stopper, reflux condenser, an addition funnel, and a magnetic stir bar. The system was flame-dried and flushed with nitrogen. Anhydrous ether (10 mL) was introduced to cover the magnesium. As the contents of the flask were stirred, iodomethane (8.28 mL,

132.9 mmol) in 60 mL of anhydrous ether was added dropwise through the addition funnel, over a period of 2 hours. The mixture was then stirred for an additional hour and cooled to 0 °C. 1-indanone (10.86 g, 80 mmol) in anhydrous ether (50 mL) was added dropwise to previously made methylmagnesium iodide. After addition of 1-indanone, the mixture was allowed to warm to room temperature and stirred. The mixture was then subjected to reflux for 1.5 hours. The crude mixture was cooled to room temperature and water (20 mL) was added at 0°C. The crude mixture was extracted with diethyl ether (3 x 30 mL). Combined ether layers were washed with water (20 mL), dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure to afford 1-hydroxl-1-methylindene (8.81 g, 81% mass recovery). The formation of the product was confirmed by IR analysis.

3-Methylindene (**49**)

A 250 mL round-bottom flask, equipped with magnetic stir bar, reflux condenser, and dean-stark apparatus, containing 1-hydroxl-1-methylindene (8.81 g, 59.4 mmol) was charged with dichloromethane (100 mL) and *p*-toluenesulfonic acid (0.4g, 2.3 mmol). The solution was stirred for 1.5 hours at room temperature, and then subjected to reflux for about 1 hour. The reaction was cooled down to room temperature and neutralized with sodium methoxide (200 mg, 3.7 mmol). Sodium methoxide was removed via gravity filtration. Solvent was removed under reduced pressure. A simple distillation of a crude mixture at 80°C (0.5 torr) afforded 1-methylindene as yellow liquid (3.86 g, 50 %). ^1H NMR (400 MHz,$CDCl_3$) δ7.65 (d, 1H, J=7.6Hz), δ 7.53 (m, 2H, J=7.8Hz), δ 7.42 (m, 1H, J=7.1Hz), δ 6.39 (s, 1H), δ 3.50 (s, 1H), δ 2.38 (s, 3H). Compared to known spectra in the literature.[108]

2-Bromo-1-Methylnaphthalene

The procedure of Pathak *et al.* was modified. [109]A 100 mL round-bottomed flask, equipped with magnetic stir bar and septum, was charged with anhydrous potassium *tert*-butoxide (3.1 g, 28 mmol) and diethyl ether (40 mL). Redistilled 1-methylindene (3.0 g, 23 mmol) was added dropwise under nitrogen atmosphere to yield dark pink slurry. Purified methyl bromide (7.35 g, 29.0 mmol) was added dropwise over a period of 35 minutes. The color of the viscous mixture became pink, then dark purple and finally dark orange. The reaction was stirred overnight under nitrogen atmosphere. The mixture was quenched with water (50 mL) and extracted with diethyl ether (3 x 50 mL). Combined ether layers were washed with brine (30 mL). The mixture was filtered via vacuum filtration and ether layer was dried over $MgSO_4$ and filtered. Solvent was removed under reduced pressure to yield brown oil. The oil was slurred with absolute ethanol (56 mL) and potassium hydroxide (800 mg, 14.3 mmol) and refluxed for one hour. Hexane (75 mL) was added and the mixture was refluxed for 30 minutes, and then filtered via vacuum filtration. The mixture was washed with hexane (3 x 50 mL) and solution was evaporated on a rotary evaporator. The crude mixture was purified by column chromatography with hexane to afford 2-bromo-1-methylnaphthalene as yellow oil (637 mg, 47 %).^{1}H NMR (400 MHz, $CDCl_3$) δ:7.94 (d, 1H, J=8.3Hz), 7.73 (d, 1H, J=9.4Hz), 7.54 (d, 1H, J=8.8Hz), 7.45 (m, 3H), 2.72 (s, 3H);^{13}C NMR (400MHz,$CDCl_3$) δ: 133.7, 133.6, 132.7, 130.4, 128.9, 127.8, 127.0, 126.0, 124.7, 122.9, 19.1. Compared to known spectra in the literature.[110]

1-Trimethylsylil (ethynyl)-2-methylnaphthalene

The procedure of Erdélyi and Gogoll was modified.[37] A 5 mL microwave vial, equipped with magnetic stir bar and septum, was charged with 2-bromo-1-methylnaphthalene (245 mg, 1.1 mmol) and (trimethylsilyl) acetylene (120 mg, 1.2 mmol). Dimethylformamide (1 mL) and triethylamine (3 mL) were added to the vial via syringe under nitrogen atmosphere. The vial was purged with nitrogen under the vacuum (0.5 torr). Tetrakis(triphenylphosphine)palladium(0) (64 mg, 0.06mmol), copper iodide (11 mg, 0.06 mmol), and triphenylphosphine (52 mg, 0.20 mmol) were added to the mixture. The vial was purged with nitrogen. The reaction was run in the CEM microwave reactor, closed vessel, at 120 °C/50W for 1 hour. The crude mixture was poured over 0.1M HCl (20-25 mL) and extracted with diethyl ether (3x15 mL). The combined organic layers were washed with saturated solution of $NaHCO_3$ (2x15-20 ml) and water (2x 15-20 ml). The combined organic layers were dried over $MgSO_4$ and filtered. The crude mixture was diluted with hexane to remove remaining triphenylphosphine and filtered. The solvent was removed under reduced pressure to afford 2-trimethylsylil (ethynyl)-1-methylnaphthalene as brown oil (220 mg, 90% mass recovery).

2-Ethynyl-1-Methylnaphthalene (**55**)

A 25 mL round-bottomed flask, equipped with magnetic stir bar and septum, was charged with 2-trimethylsylil (ethynyl)-1-methylnaphthalene (220 mg, 0.9 mmol), anhydrous potassium fluoride (218 mg, 4.0 mmol) and methanol (2 mL). The reaction was stirred at room temperature four days and monitored by TLC. The crude mixture was diluted with water (10 mL) to dissolve remaining potassium fluoride, followed by the extraction with diethyl ether (3x 15 mL). Combined ether layers were washed with water (10 mL), dried

over $MgSO_4$ and filtered. Column chromatography eluting with hexanes afforded the pure 2-ethynyl-1-methylnaphthalene as yellow oil (72 mg, 50%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, 1H, J=8.1Hz), 7.85 (d, 1H, J=8.5Hz), 7.69 (d, 1H, J=8.5Hz), 7.56 (m, 3H), 3.44 (s, 1H), 2.92 (s, 3H); ^{13}C NMR(400 MHz, $CDCl_3$) δ: 138.5, 133.5, 132.5, 129.2, 128.8, 126.7, 126.4, 124.8, 119.3, 84.0, 81.6, 17.2.

Sodium Borohydride reduction of α-Tetralone

A 25 mL round-bottomed flask, equipped with magnetic stir bar, was charged with α-tetralone (2.1 g, 13.7 mmol) and 10 mL of methanol. The flask was cooled to 0 °C and sodium borohydride (262 mg, 6.9 mmol) was added in portions. Reaction mixture started fizzing. After fizzing ceased, the flask was warmed up to room temperature and stirred for 20 minutes. The crude reaction mixture was quenched with 3M sodium hydroxide (5mL) and water (5mL), followed by extraction with dichloromethane (3x15mL). Combined organic layers were washed with water, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure to afford α-tetralol as a clear liquid (2.07g, 96%). Used without further purification.

Synthesis of 1,2-Dihydronaphthalene (**45**)

A 500 mL round-bottomed flask, equipped with magnetic stir bar and septum, was charged with α-tetralol (1.0 g, 6.8 mmol) and dichloromethane (300mL) via syringe under nitrogen atmosphere. *p*-Toluenesulfonic acid monohydrate, $TsOH{\cdot}H_2O$, (65mg, 5mol%) was added to the mixture. The reaction stirred at the room temperature for 24 hours under nitrogen atmosphere. The reaction was quenched with saturated $NaHCO_3$ (40mL) and the color of the mixture changes form light purple to light yellow. Organic layer was washed with saturated $NaHCO_3$ (2x50mL), water (40 mL), dried over Na_2SO_4

filtered. The solvent was removed under reduced pressure to afford 1,2-dihydronaphtahlene as a yellow liquid (855 mg, 85%).

Synthesis of 2-Vinyltoluene (**40**)

The procedure of Okamoto *et al.* was modified.[111] A 100 mL round-bottomed flask, equipped with magnetic stir bar and septum, was charged with CH_3PPh_3Br (4.3 g, 12 mmol) and dissolved in dry tetrahydrofuran (50 mL). The mixture was cooled to -78 °C before adding 1.6 M n-butyllithium (9.4 mL, 15 mmol) via syringe over 10 minute period. The color of the mixture changed from cloudy to bright yellow. The reaction was stirred for 30 minutes at room temperature under nitrogen atmosphere, and color of the mixture changed to dark orange, and then to dark brown over time. After 30 minutes, the mixture was cooled down to 0°C and o-toluylaldehyde (1.2 mL, 10 mmol) was added via syringe. The reaction was stirred at room temperature for 24 hours. The reaction was quenched by adding diethylether (10mL) and hexanes (15mL). The precipitate was filtered through a silica plug using a fine fritted funnel. The solvent was removed under reduced pressure. The crude mixture was purified by column chromatography with pentane to afford pure 2-vinyltoluene as colorless liquid (1.12 g, 95%). ^1H and ^{13}C NMR data were compared to reported data in the literature.[112]

Synthesis of 1-(2-Methylphenyl)propyne (**51**)

The procedure of Buck and Chong was modified.[113]A 100 mL round-bottomed flask, equipped with magnetic stir bar and septum, was charged with 2-ethynyltoluene (1.5 mL, 12 mmol) and tetrahydrofuran (50 mL) via syringe under nitrogen atmosphere. The reaction was cooled down to -78 °C before adding n-butyllithium (6.9 mL, 11 mmol) dropwise via syringe. The color of the mixture turned yellow. The reaction was stirred

for 40 minutes. The reaction mixture was warmed to room temperature and iodomethane (1.5 mL, 24 mmol) was added to the flask. The reaction was stirred for 24 hours at the room temperature under nitrogen atmosphere. The reaction was cooled to 0 °C and quenched with saturated ammonium chloride. A white solid that precipitate out was removed by vacuum filtration. The crude mixture was extracted with diethyl ether (3x10mL). Combined organic layers were washed with saturated ammonium chloride (3x10mL), dried over $MgSO_4$ and filtered. The crude mixture was concentrated under reduced pressure and purified by Kugelrohr distillation to afford pure 2-prop-1-ynyl-toluene as viscous colorless oil (988 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 1H), 7.26 (dt, *J* = 5.4, 1.3 Hz, 2H), 7.22 – 7.17 (m, 1H), 2.53 (s, *J* = 1.8 Hz, 4H), 2.18 (s, *J* = 1.3 Hz, 3H).^{13}C NMR (400 MHz, $CDCl_3$) δ 140.19, 132.15, 129.60, 127.80, 125.74, 124.17, 89.90, 78.98, 20.98, 4.67. Compared to known data in the literature.[114]

Pyrolysis of 1-Ethynyl-2-methylnaphthalene

1-Ethynyl-2-methylnaphthalene (**54**,33mg, 0.20mmol) and graphite (75 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen and sealed. Pyrolysis was carried out in a CEM reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. The crude mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated to yield brown solid in 52 % mass recovery. ^{1}H NMR analysis of the crude mixture showed 1:1 mixture of 1*H*-benzo[e]indene and 3*H*-benzo[e] indene.

Pyrolysis of 2-Ethynyl-1-methylnaphthalene

2-Ethynyl-1-methylnaphthalene (**55**, ~20mg, 0.12mmol) and graphite (85 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above graphite. The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen and sealed. Pyrolysis was carried out in a CEM reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. The crude mixture was extracted with dichloromethane, filtered through neutral alumina and concentrated to yield brown solid in 45 % mass recovery. ^{1}H NMR analysis of the crude mixture showed 1:1 mixture of 1*H*-benzo[e]indene and 3*H*-benzo[e] indene

Flash Vacuum Pyrolysis of 1-Acetylnaphthalene

1-Acetylnaphthalene (**61**,222 mg, 1.30 mmol) was passed through a horizontal quartz tube maintained at 880 °C evacuated to pressure of 0.03 torr over 30 minutes. The product mixture condensed in a trap cooled with dry ice. At the end of the reaction, the vial was flushed with nitrogen and crude mixture was extracted with dichloromethane. Solvent was removed under reduced pressure to yield light brown oil in 71% mass recovery. Components in the crude mixture were analyzed by ^{1}H NMR and identified by comparison to authentic samples. Capillary GC analysis gave the percent of each component in the crude mixture: naphthalene (**2**, 42%), 1-methylnaphthalene (**66**, 13%), 2-methylnaphthalene (**65**, 3%), and starting material (**61**, 41%).

Pyrolysis of 1-Acetylnaphthalene with Tungsten Oxide (WO_3)

1-Acetylnaphthalene (**61**, 57 mg, 0.33 mmol) and tungsten oxide (134 mg) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the mixture.

The quartz tube was inserted into a Pyrex microwave reaction tube, purged with nitrogen and sealed. Pyrolysis was carried out in a CEM reactor using dynamic power mode at 300 °C/150 W for five minutes ramp time and one minute hold time. The crude mixture was extracted with $CDCl_3$, filtered through neutral alumina and subjected to NMR analysis. Analysis by 400 MHz ^1H NMR showed only starting material.

Pyrolysis of 1-Acetylnaphthalene with Tungsten Oxide (WO_3) and Graphite

1-Acetylnaphthalene (**61**, 61 mg, 0.33 mmol), tungsten oxide (150 mg), and graphite (31 mg; Aldrich synthetic graphite, 20 microns) were mixed using a mortar in a quartz tube (12 x 70 mm).Reaction was run "closed vessel" as above at 300 °C/150 W for one minute hold time. The crude mixture was extracted with $CDCl_3$, filtered through neutral alumina and subjected to NMR analysis. Analysis by 400 MHz ^1H NMR showed the mixture to be 40% naphthalene (**2**), 17% 1-acenaphthone (**63**), and 44% starting material.

Pyrolysis of 1-Acetylnaphthalene with Graphite

1-Acetylnaphthalene (**61**, 56 mg, 0.33 mmol) and graphite (106 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm).). Reaction was run "closed vessel" as above at 300 °C/150 W for one minute hold time. The crude mixture was extracted with $CDCl_3$, filtered through neutral alumina and subjected to NMR analysis. Analysis by 400 MHz ^1H NMR showed the mixture to be 25 % naphthalene (**2**), 20% 1-acenaphthone (**63**), and 55% starting material.

Pyrolysis of 2-Acetylnaphthalene with Tungsten Oxide (WO_3) and Graphite

2-Acetylnaphthalene (**64**, 58 mg, 0.34 mmol), tungsten oxide (151 mg), and graphite (32 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm). A small plug of glass wool was placed above the mixture. The quartz tube was inserted into

a Pyrex microwave reaction tube, purged with nitrogen, and sealed. Pyrolysis was carried out in a CEM reactor using dynamic power mode at 300°C/150 W for five minutes ramp time and one minute hold time. The crude mixture was extracted with $CDCl_3$, filtered through neutral alumina and subjected to NMR analysis. Analysis by 400 MHz ^{1}H NMR showed only starting material.

Pyrolysis of 2-Acetylnaphthalene with Graphite

2-Acetylnaphthalene (**64**, 34 mg, 0.20 mmol) and graphite (97 mg; Aldrich synthetic graphite, 20 microns) were mixed in a quartz tube (12 x 70 mm).). Reaction was run "closed vessel" as above at 300 °C/150 W for one hold time. The crude mixture was extracted with $CDCl_3$, filtered through neutral alumina and subjected to NMR analysis. Analysis by 400 MHz ^{1}H NMR showed the mixture to be 20 % naphthalene (**2**), 13% 2-methylnaphthalene (**65**), and 60% starting material.

Flash Vacuum Pyrolysis of 2-Acetylnaphthalene

2-Acetylnaphthalene (**64**, 114 mg, 0.67 mmol) was passed through a horizontal quartz tube maintained at 900 °C evacuated to pressure of 0.03 torr over 30 minutes. The product mixture condensed in a trap cooled with dry ice. At the end of the reaction, the vial was flushed with nitrogen and crude mixture was extracted with dichloromethane. Solvent was removed under reduced pressure to yield dark yellow oil in 65% mass recovery. Components in the crude mixture were analyzed by ^{1}H NMR and identified by comparison to authentic samples. Capillary GC analysis gave the percent of each component in the crude mixture: naphthalene (**2**, 30%), 1-methylnaphthalene (**66**, 2%), 2-methylnaphthalene (**65**, 7%), and starting material (**64**, 60%).

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APPENDICES

APPENDIX A: Computational Data

Chapter III

Computational Data on Dehydro-Diels-Alder Reactions

Enyne- Ene Cycloadditions

Structure	E_{TOT} (DFT)	ZPVE	$E_{CCSD(T)}$
Vinylacetylene	-154.688162	0.062203	-154.3482772
Ethylene	-78.538975	0.051788	-78.3846254
1,2-Cyclohexadiene	-233.250688	0.122419	-232.7638709
Concerted **TS5**	-233.182859	0.117267	-232.6871081
Stepwise **TS 1**	-233.174588	0.114188	-232.6734504
Diradical Intermediate **R1**	-233.181904	0.113917	-232.6820157
Stepwise **TS 3**	-233.173951	0.115244	-232.6742005
Stepwise **TS 2**	-233.175712	0.113653	-232.6736078
Diradical Intermediate **R2**	-233.187538	0.113657	-232.684899
Stepwise **TS 4**	-233.177446	0.115543	-232.6776394

Enyne- Yne Cycloadditions

Structure	E_{TOT} (DFT)	ZPVE	$E_{CCSD(T)}$
Acetylene	-77.310507	0.027849	-77.1404306
1,2,4-Cyclohexatriene	-232.043294	0.098334	-231.5381154
Concerted **TS10**	-231.952616	0.09186	-231.4391951
Stepwise **TS 6**	-231.945593	0.089367	-231.4282226
Diradical Intermediate **R3**	-231.956484	0.091367	-231.441356
Stepwise **TS 8**	-231.948428	0.091087	-231.4313672
Stepwise **TS 7**	-231.947352	0.088391	-231.4288432
Diradical Intermediate **R4**	-231.962282	0.091454	-231.4436494
Stepwise **TS 9**	-231.956872	0.092029	-231.4394765

Diyne -Ene Cycloadditions

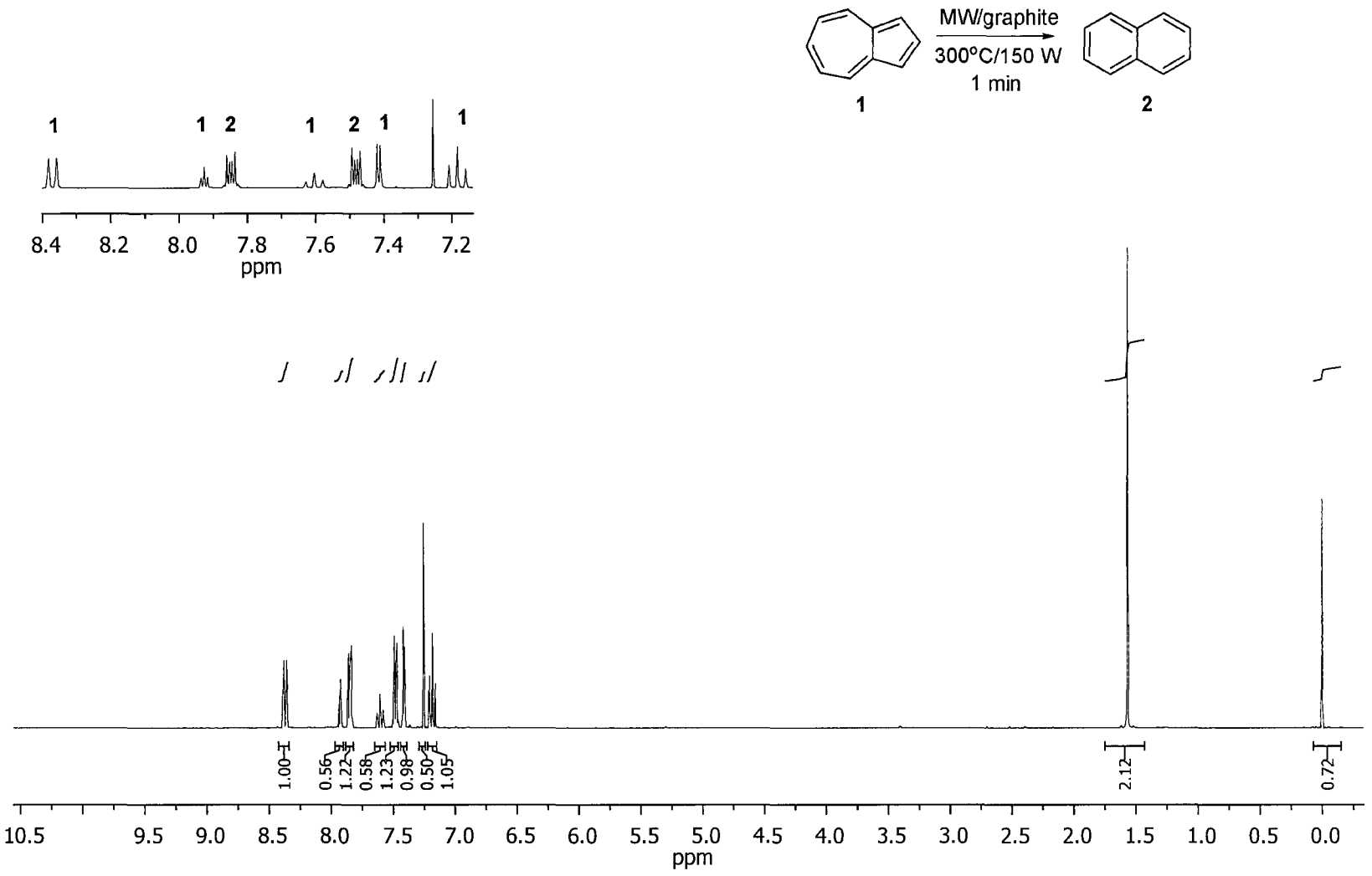
Structure	E_{TOT} (DFT)	ZPVE	$E_{CCSD(T)}$
1,3-Butadiyne	-153.461622	0.038742	-153.1049099
1,2,3- Cyclohexatriene	-232.00398	0.09817	-231.5014512
Concerted **TS13**	-231.947077	0.092693	-231.4353934
Stepwise **TS 11**	-231.949699	0.090062	-231.4299691
Diradical Intermediate **R5**	-231.958774	0.089133	-231.4362836
Stepwise **TS 12**	-231.943418	0.091592	-231.4254079

Diyne-Yne Cycloadditions

Structure	E_{TOT} (DFT)	ZPVE	$E_{CCSD(T)}$
ortho-Benzyne (**11**)	-230.861957	0.076372	-230.3369789
Concerted **TS16**	-230.716754	0.067202	-230.1878544
Stepwise **TS 14**	-230.720803	0.064729	-230.1844813
Diradical Intermediate **R6**	-230.734952	0.067404	-230.1970424
Stepwise **TS 15**	-230.726338	0.068654	-230.1903662

* All energies are reported in Hartrees

APPENDIX B: Spectra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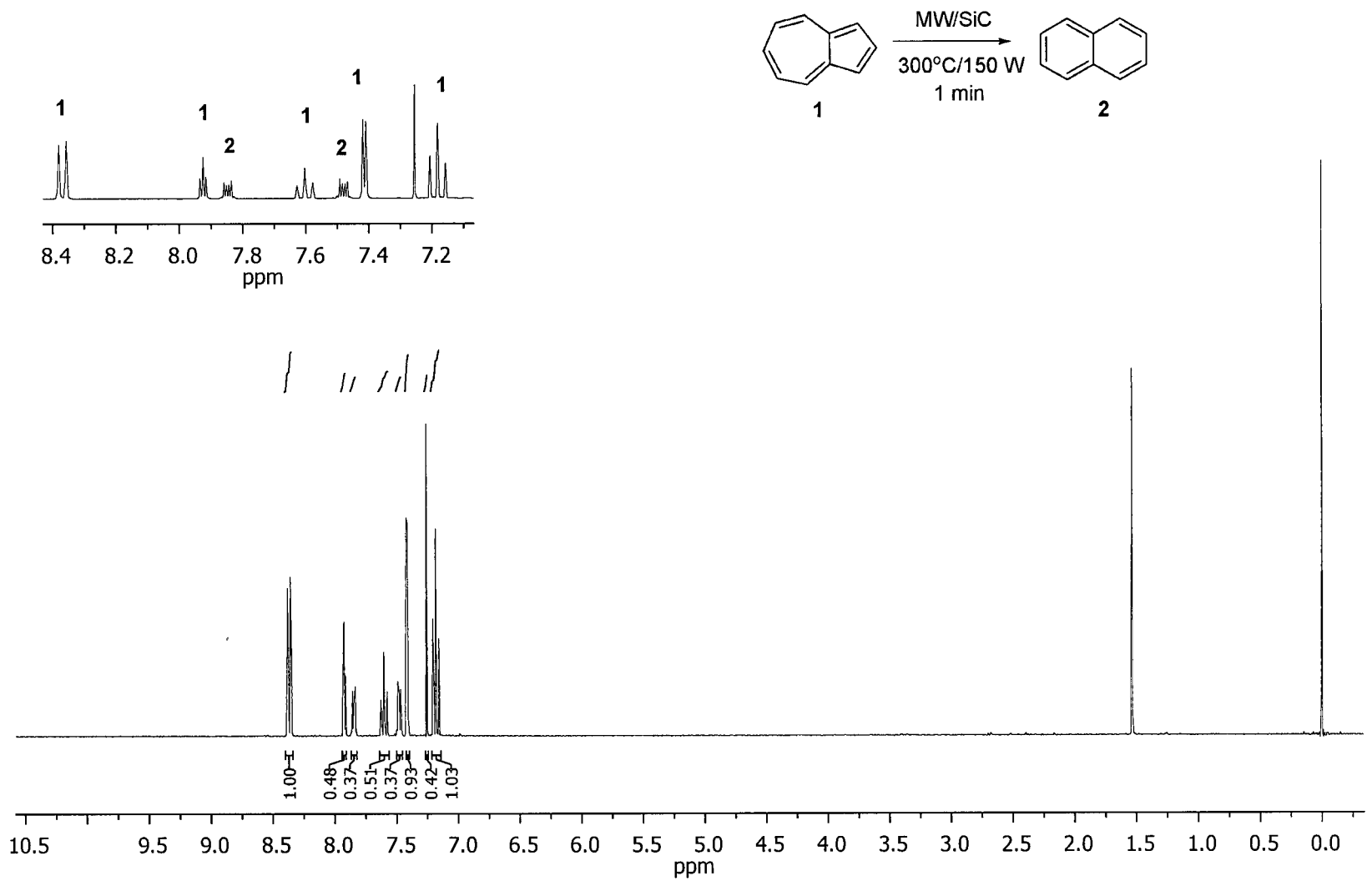
300°C/150 W
1 min
1
2
1 1 2 1 2 1 1
8.4 8.2 8.0 7.8 7.6 7.4 7.2
ppm
1.00 0.56 1.22 0.58 1.23 0.98 0.50 1.05 2.12 0.72
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


MW/SiC
300°C/150 W
1 min
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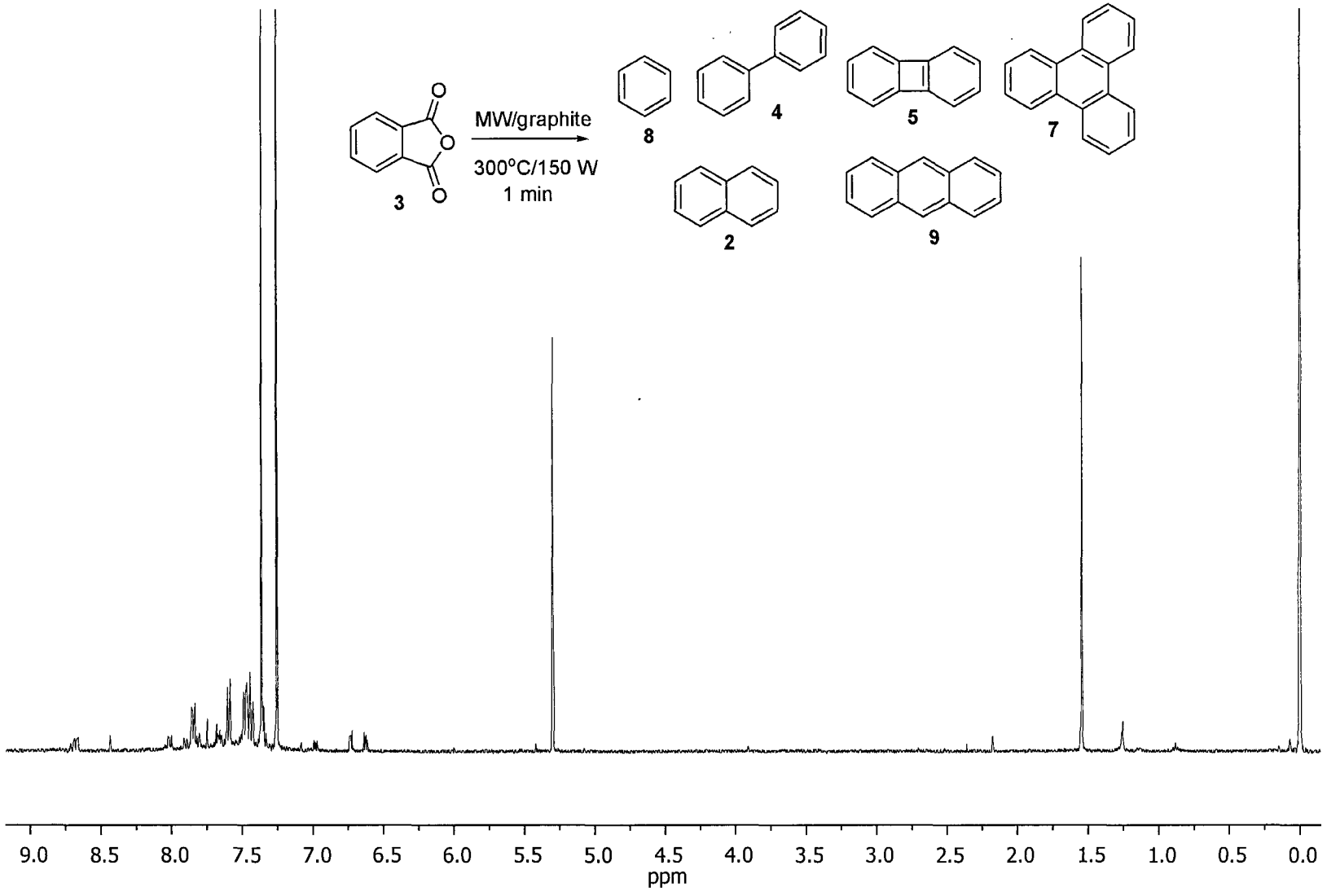
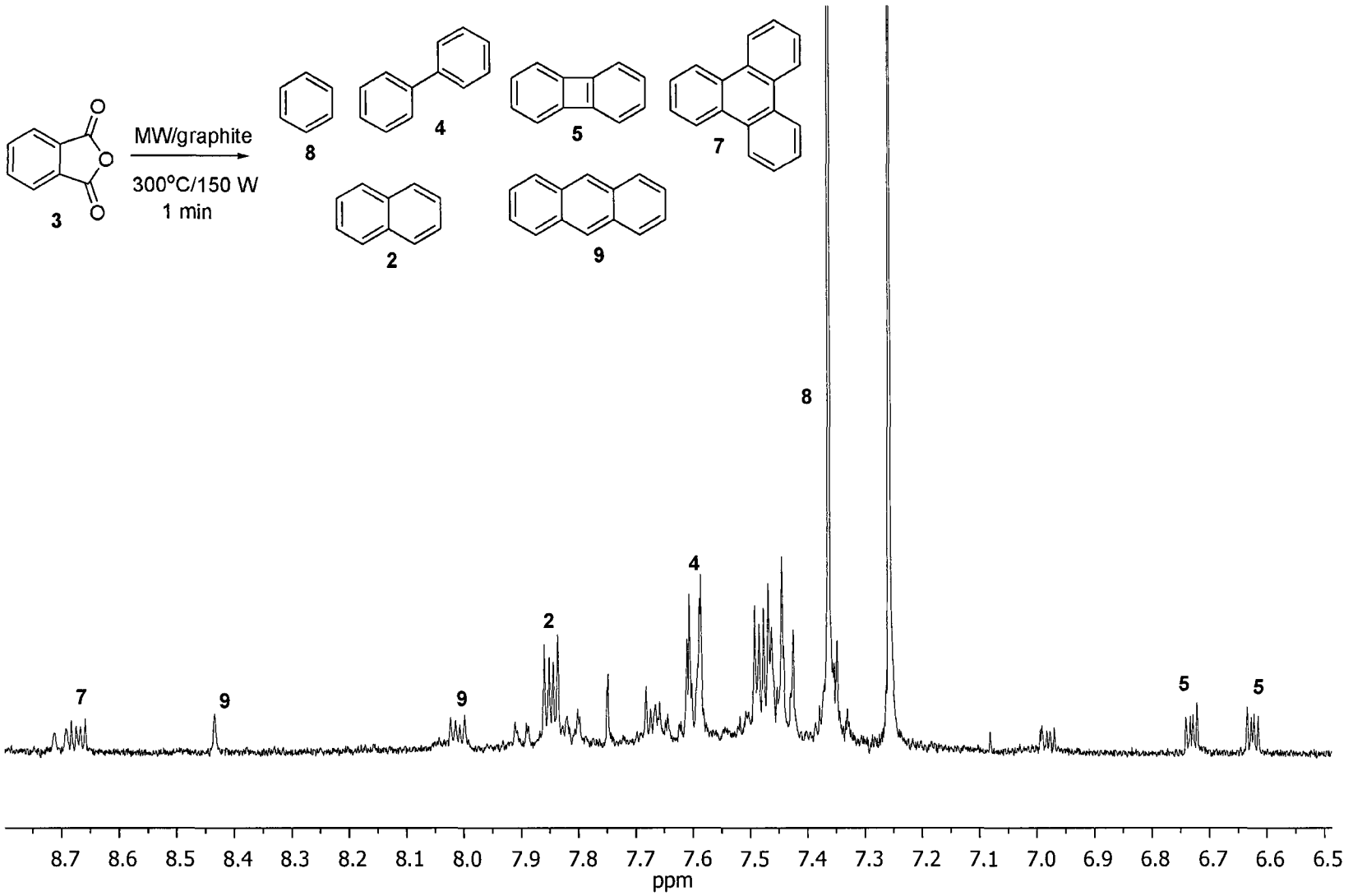
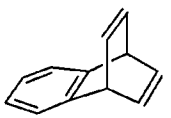
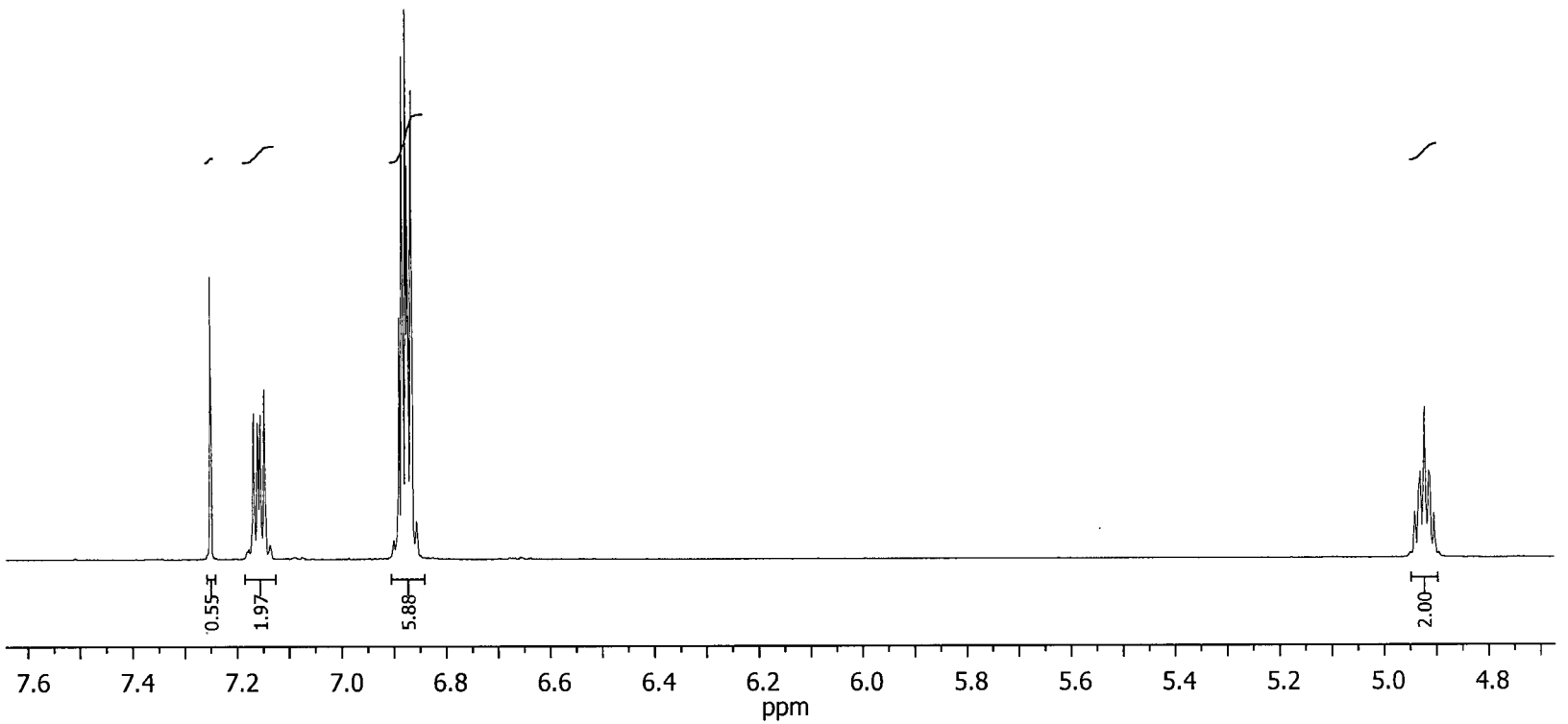
2
1
2
1
2
1
1
1
8.4
8.2
8.0
7.8
7.6
7.4
7.2
ppm
1.00
0.48
0.37
0.51
0.37
0.93
0.42
1.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

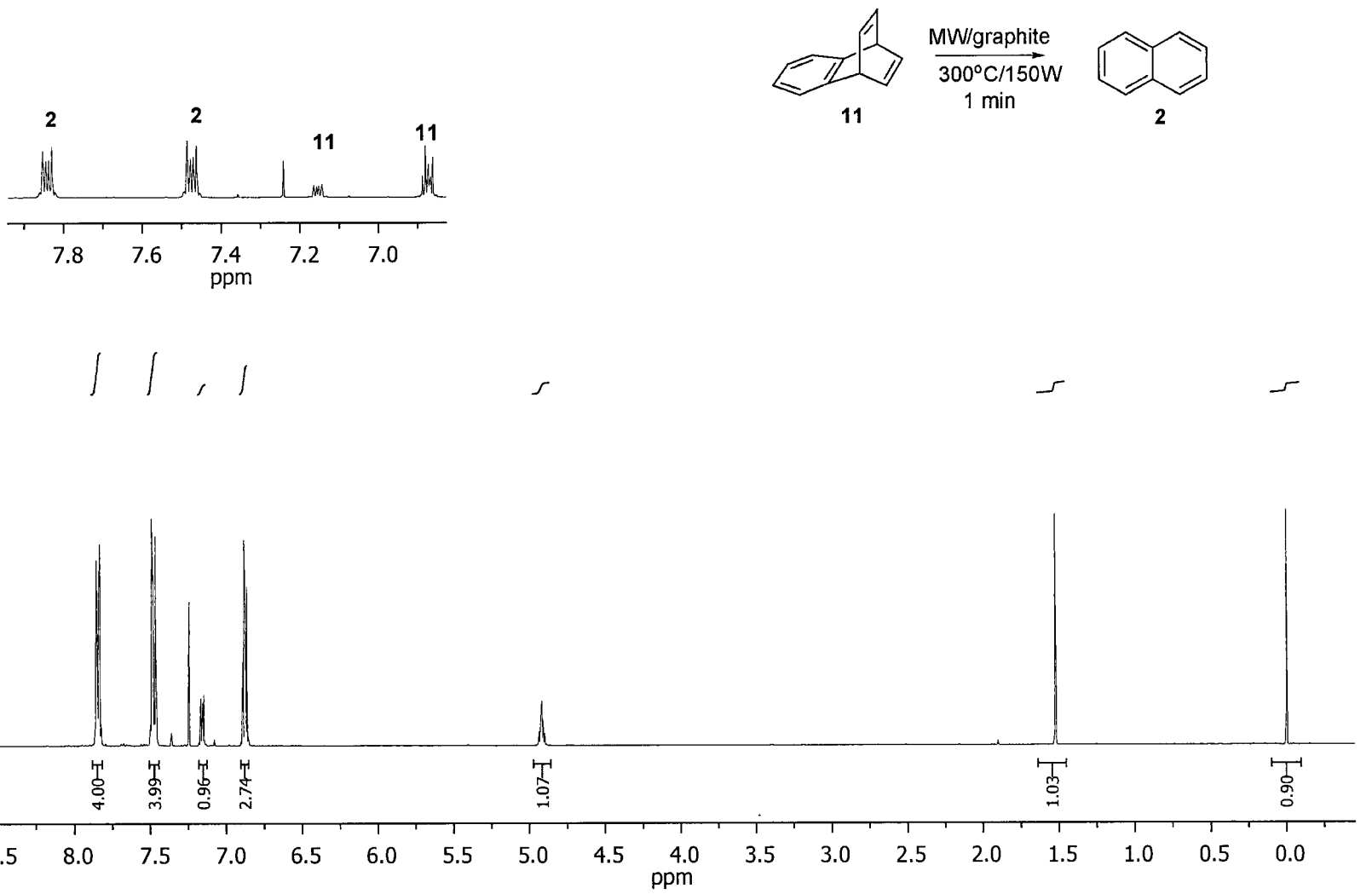

MW/graphite
300°C/150 W
1 min
3
8
4
5
7
2
9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

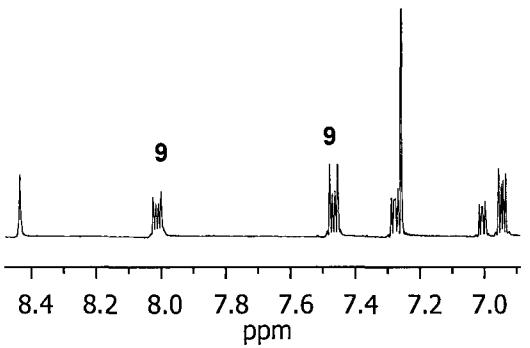

MW/graphite
300°C/150 W
1 min
3
8
4
5
7
2
9
8
4
2
7
9
9
5
5
8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5
ppm

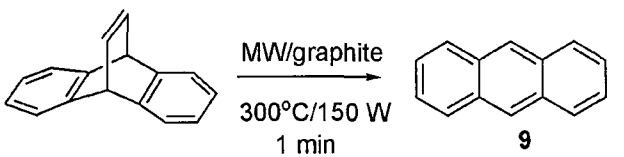


11




11
MW/graphite
300°C/150W
1 min
2
2
2
11
11
7.8
7.6
7.4
7.2
7.0
ppm
4.00
3.99
0.96
2.74
1.07
1.03
0.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


9
9
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
ppm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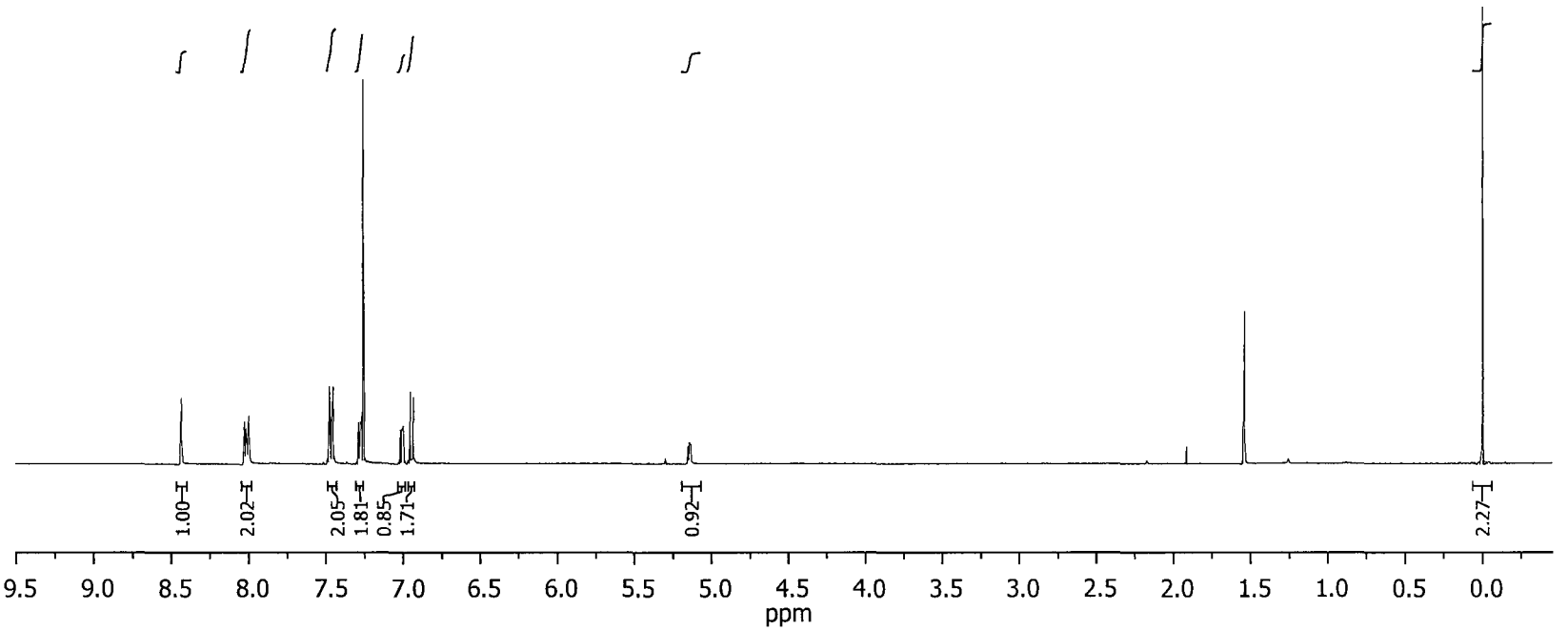
300°C/150 W
1 min
9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1.81
0.85
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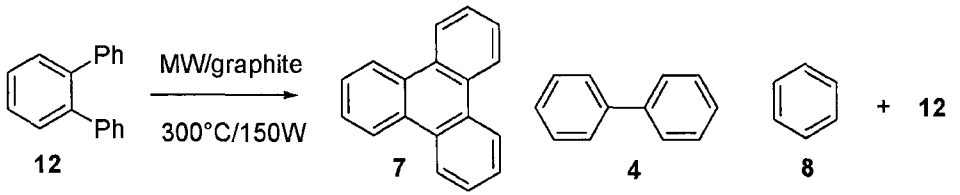
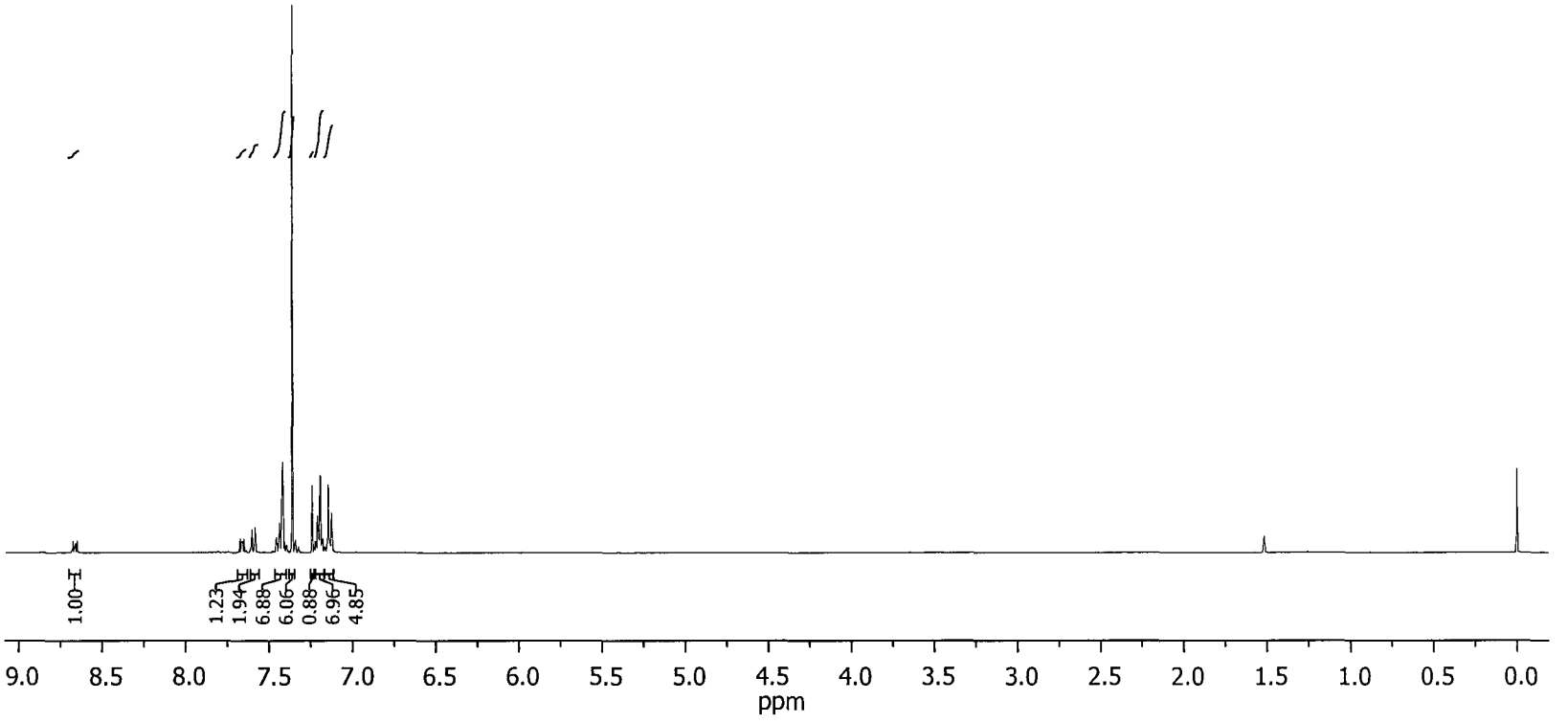
0.92
2.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Ph
Ph
MW/graphite
300°C/150W
12
7
4
8
+ 12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6.06
0.88
6.96
4.85
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8.5
8.0
7.5
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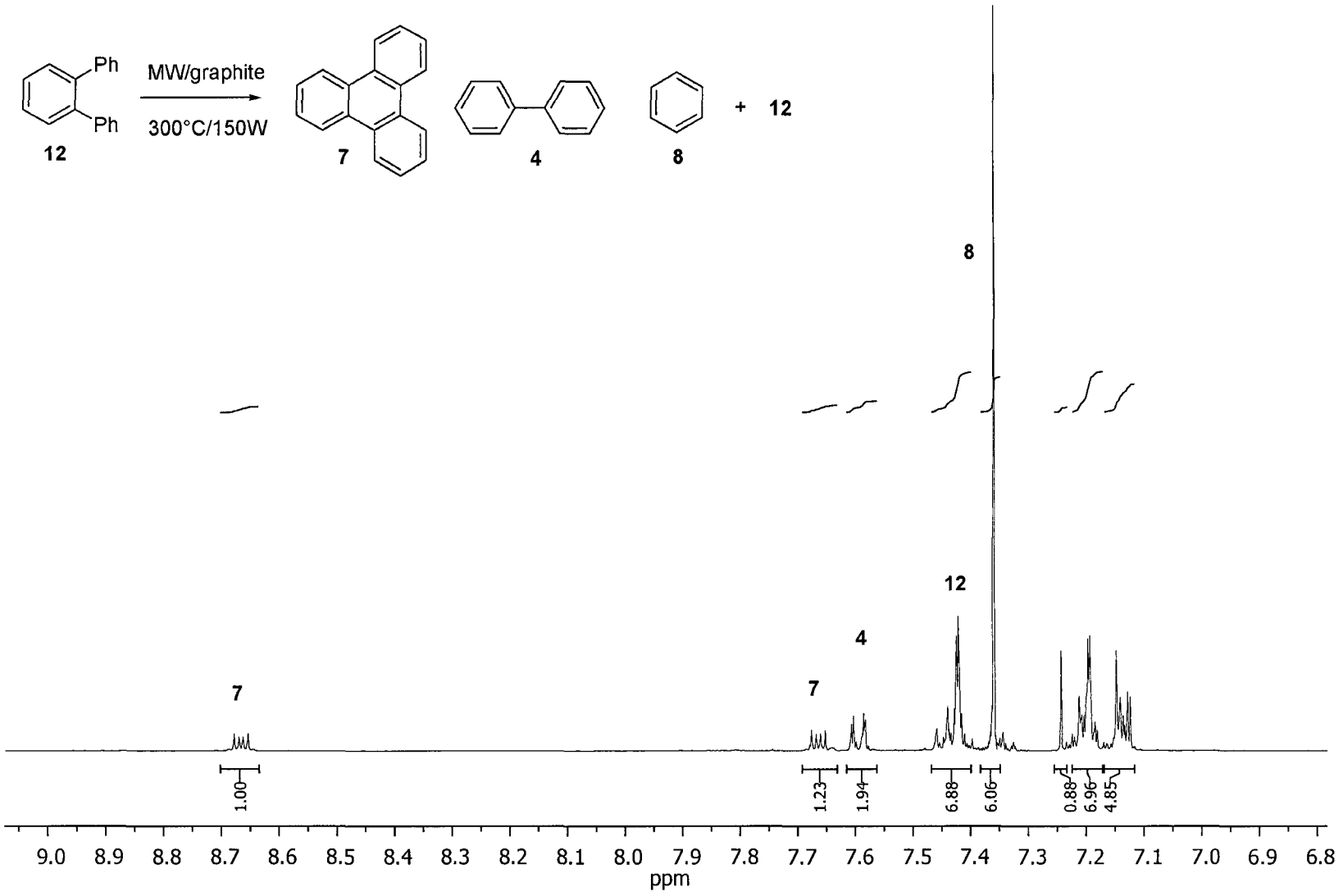
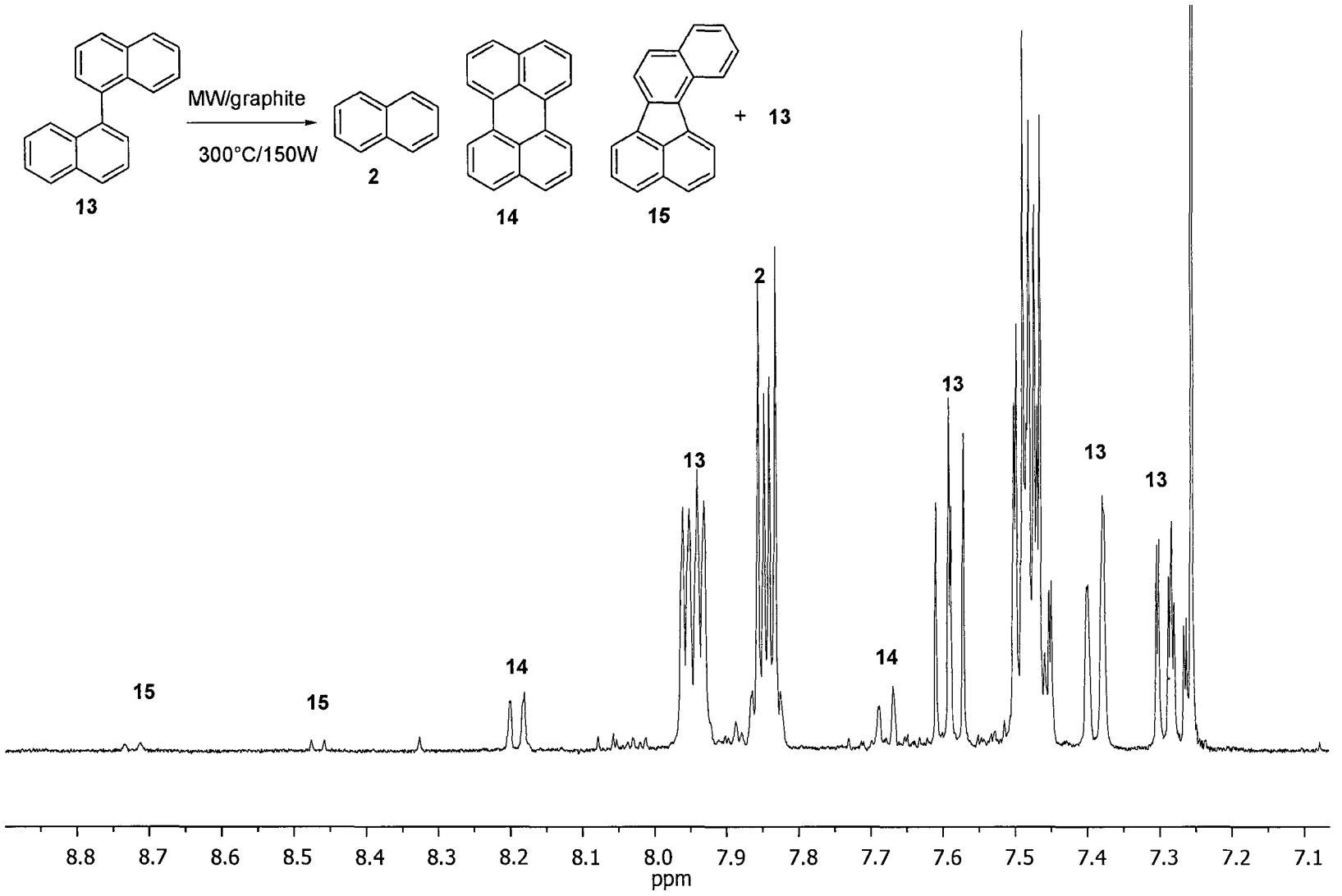
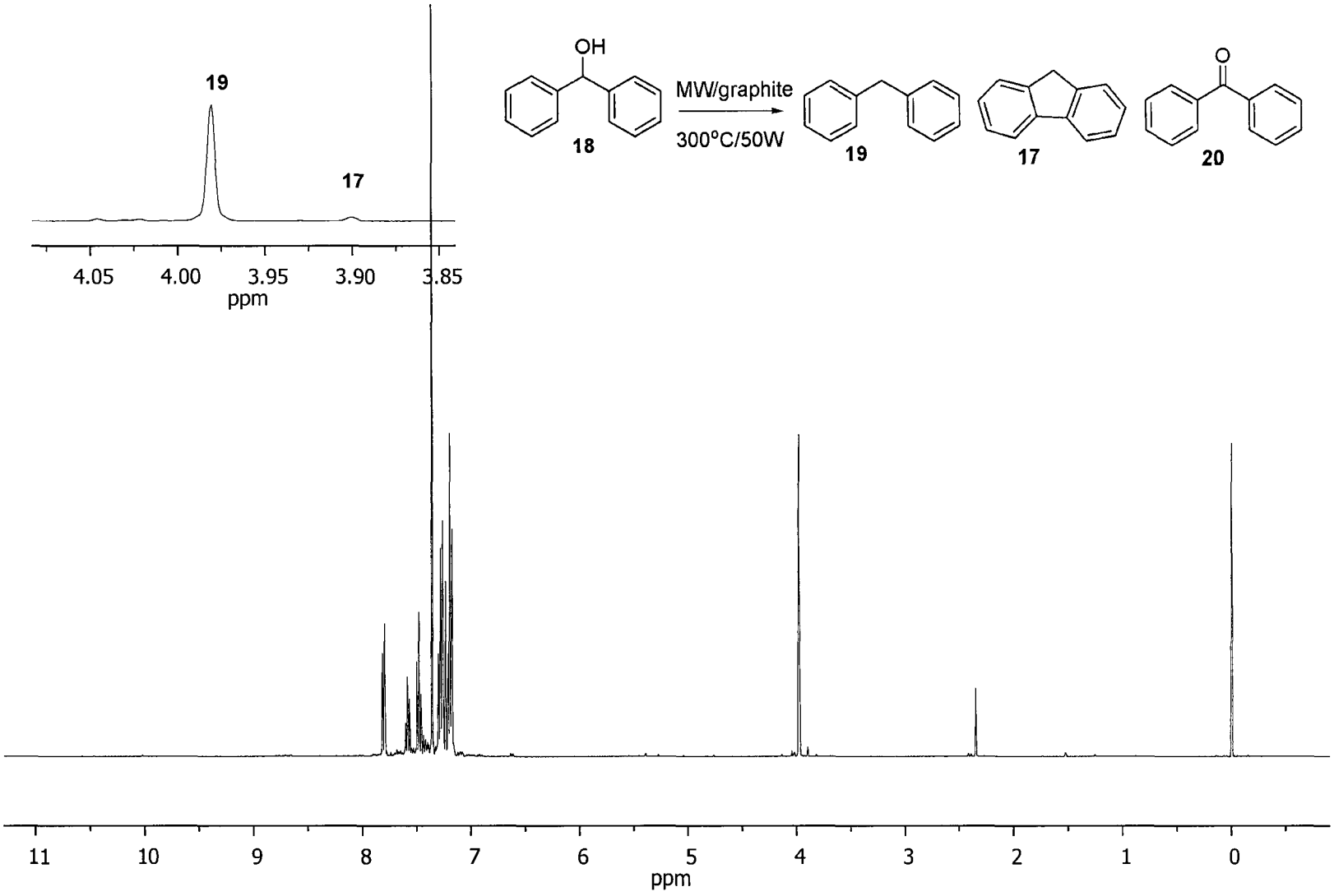
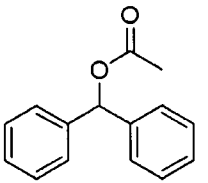
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Ph
Ph
12
MW/graphite
300°C/150W
7
4
8
+ 12
8
12
4
7
7
1.00
1.23
1.94
6.88
6.06
0.88
6.96
4.85
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
ppm

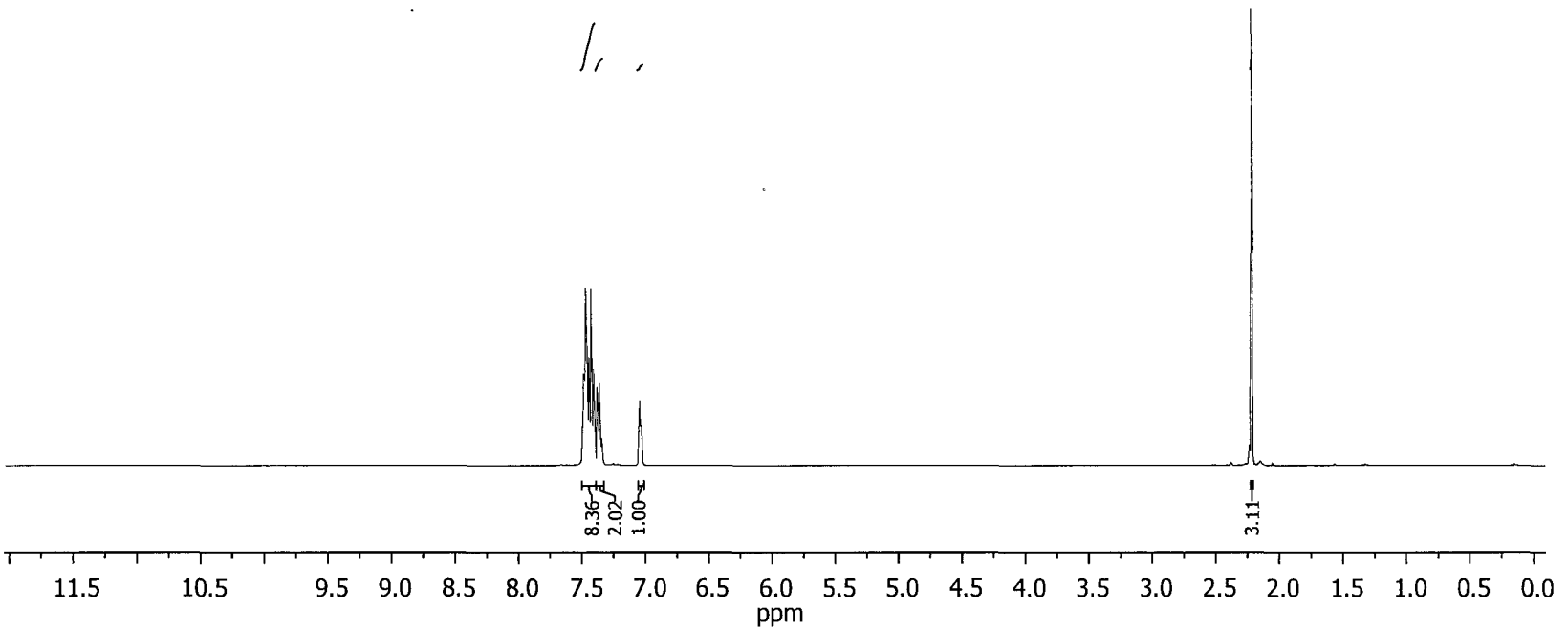
12
8
7
7
4
8.6
8.2
7.8
7.6
7.4
7.2
ppm
Ph
Ph
12
MW/WO3
300°C/150W
7
4
8
1.00
1.36
1.16
13.08
2.38
18.26
11.91
4.83
2.80
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


MW/graphite
300°C/150W
13
2
14
15
+ 13
15
15
14
13
2
14
13
13
13
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
ppm


19
17
4.05
4.00
3.95
3.90
3.85
ppm
OH
18
MW/graphite
300°C/50W
19
17
O
20
11
10
9
8
7
6
5
4
3
2
1
0
ppm



21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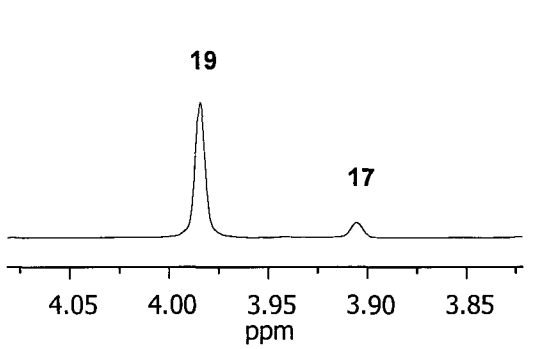
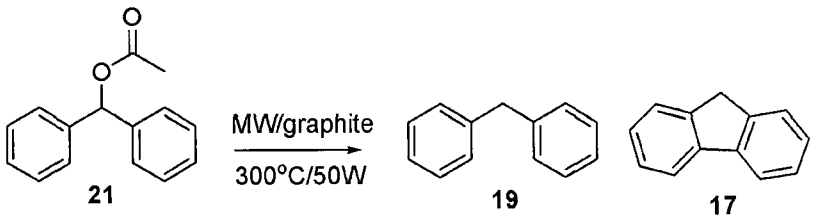
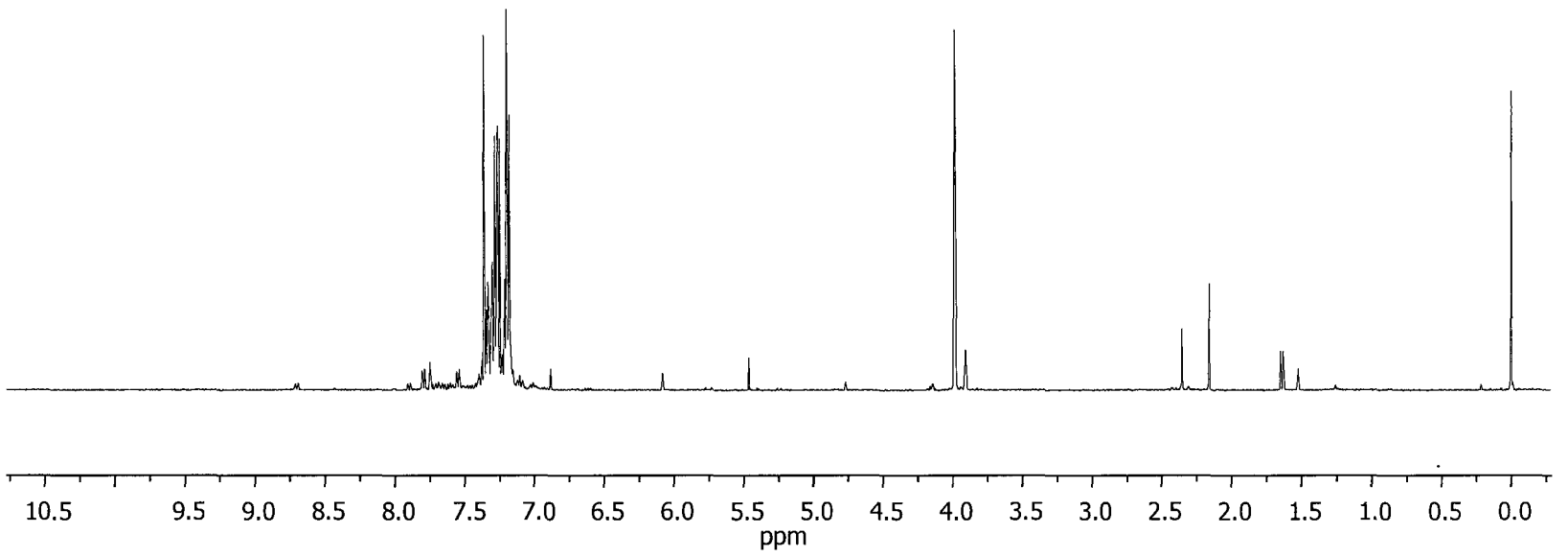
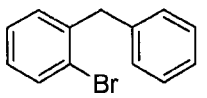
2.02
1.00
3.11
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

21
170.27
140.62
128.86
128.25
127.46
77.20
21.54
ppm

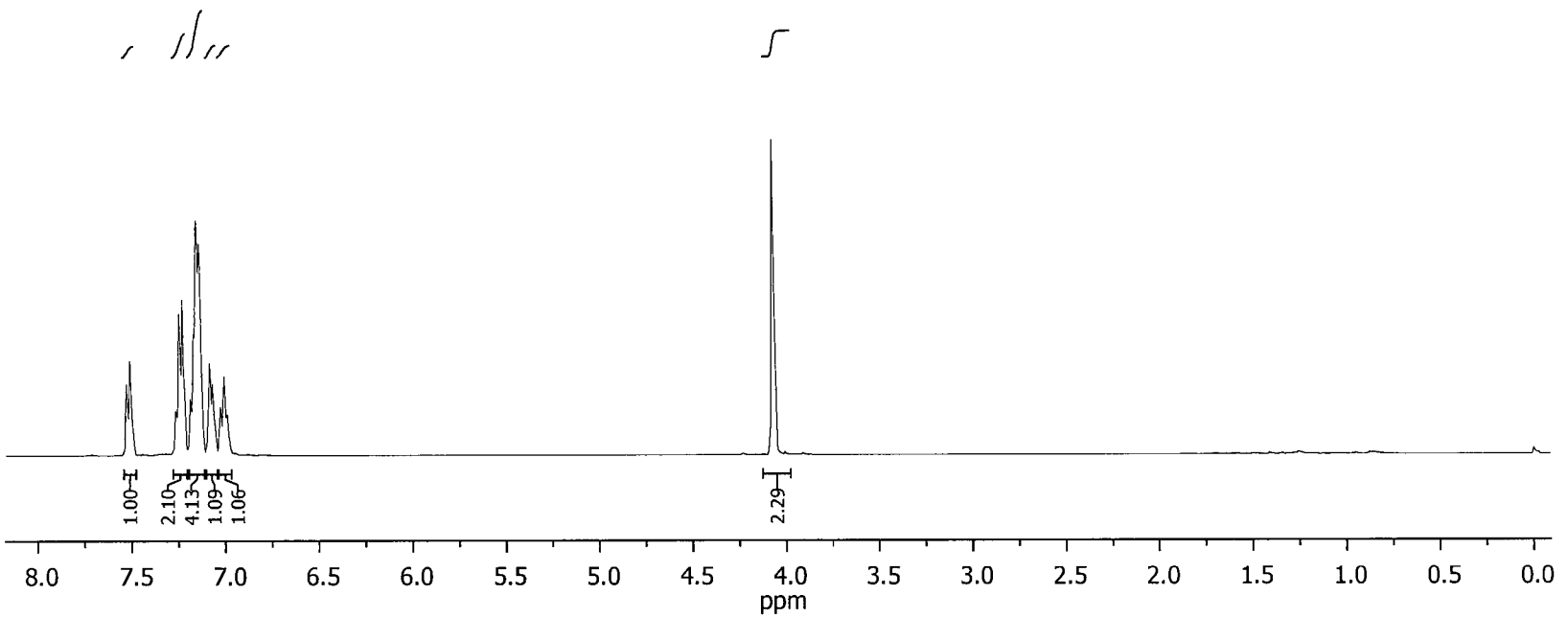

19
17
4.05
4.00
3.95
3.90
3.85
ppm

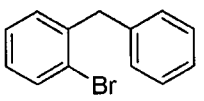

O
O
21
MW/graphite
300°C/50W
19
17


10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

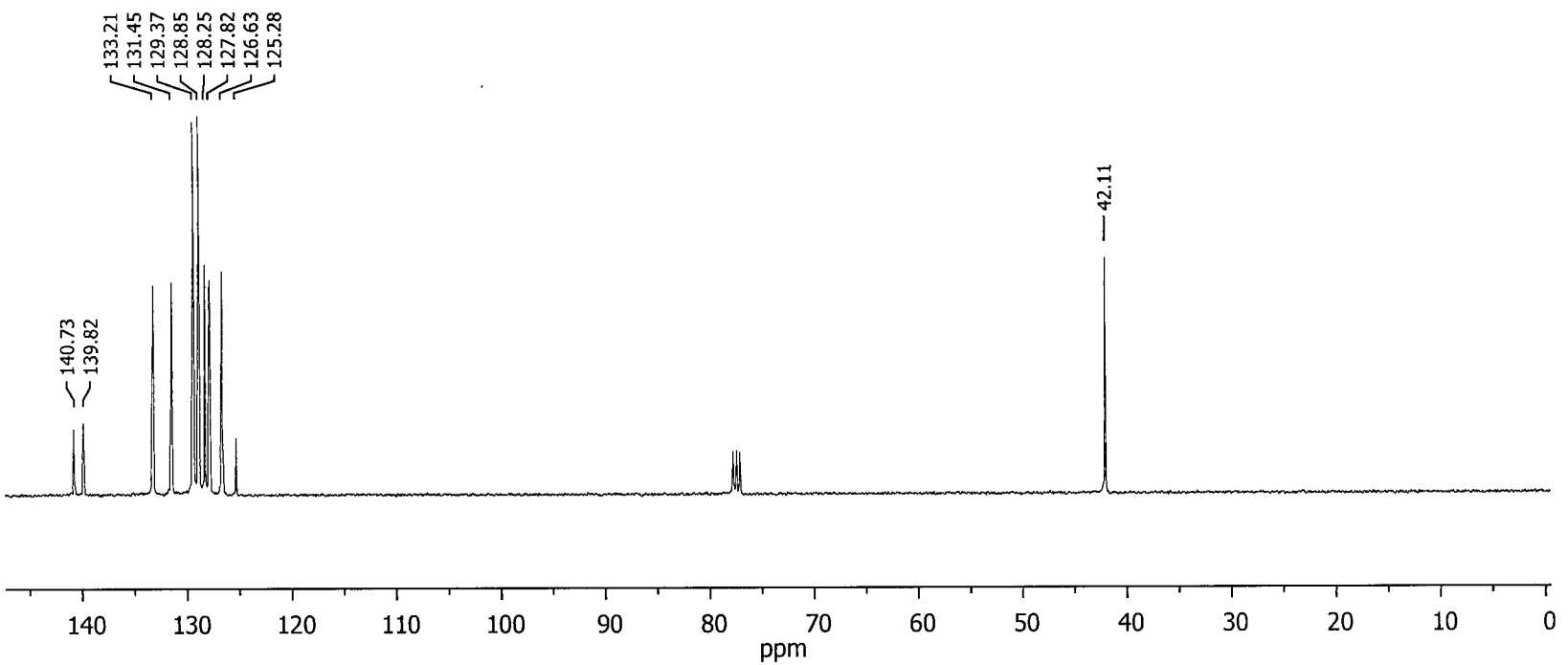

Br

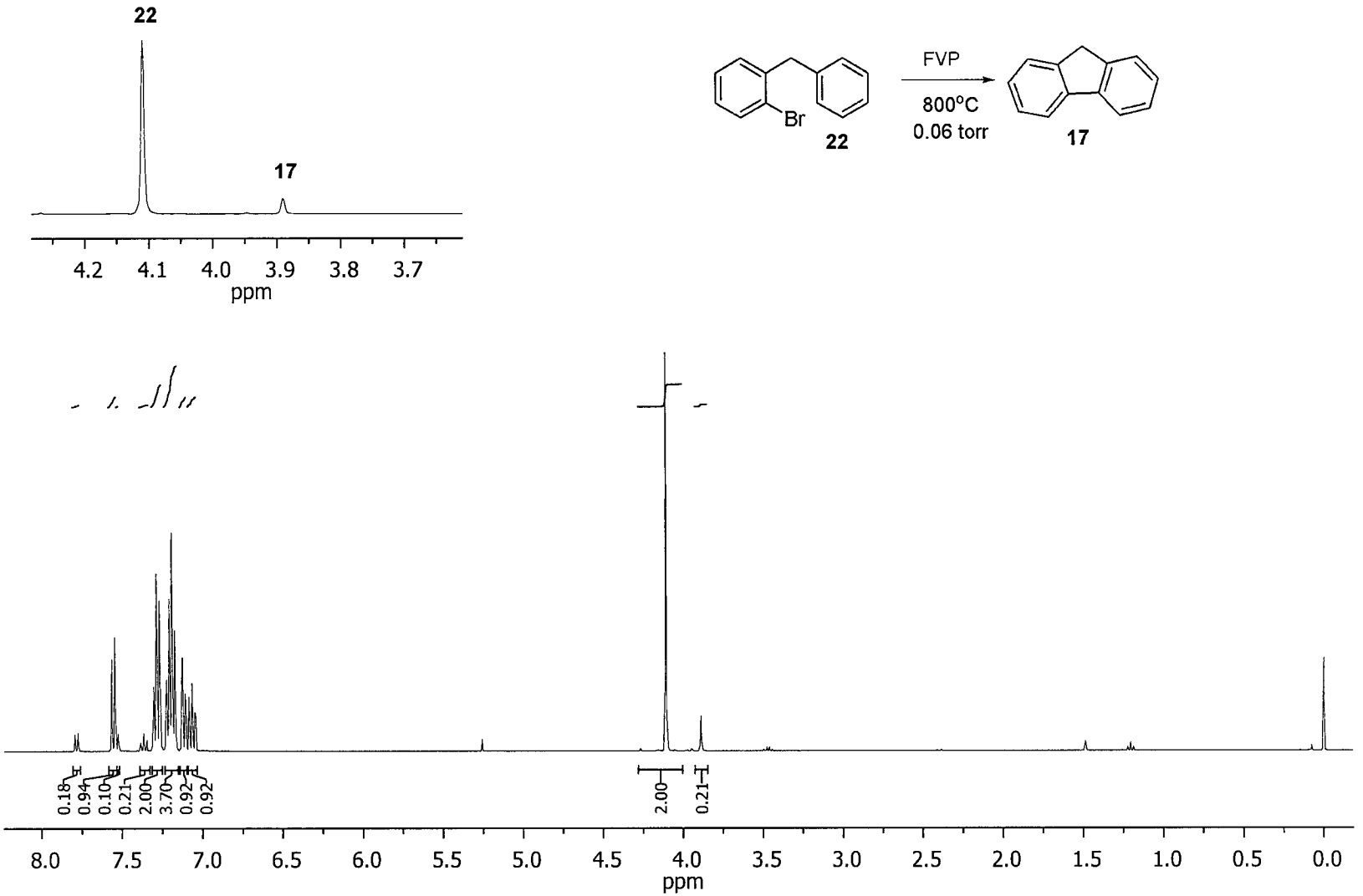
22

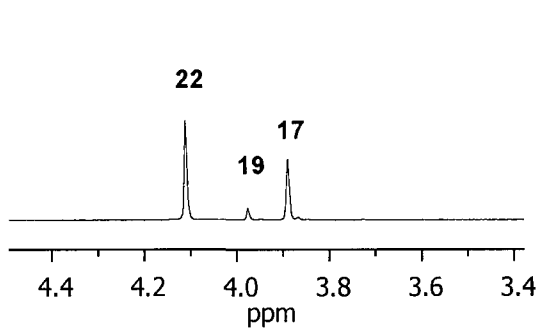

1.00
2.10
4.13
1.09
1.06
2.29
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

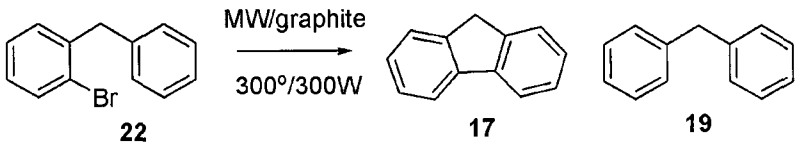

Br

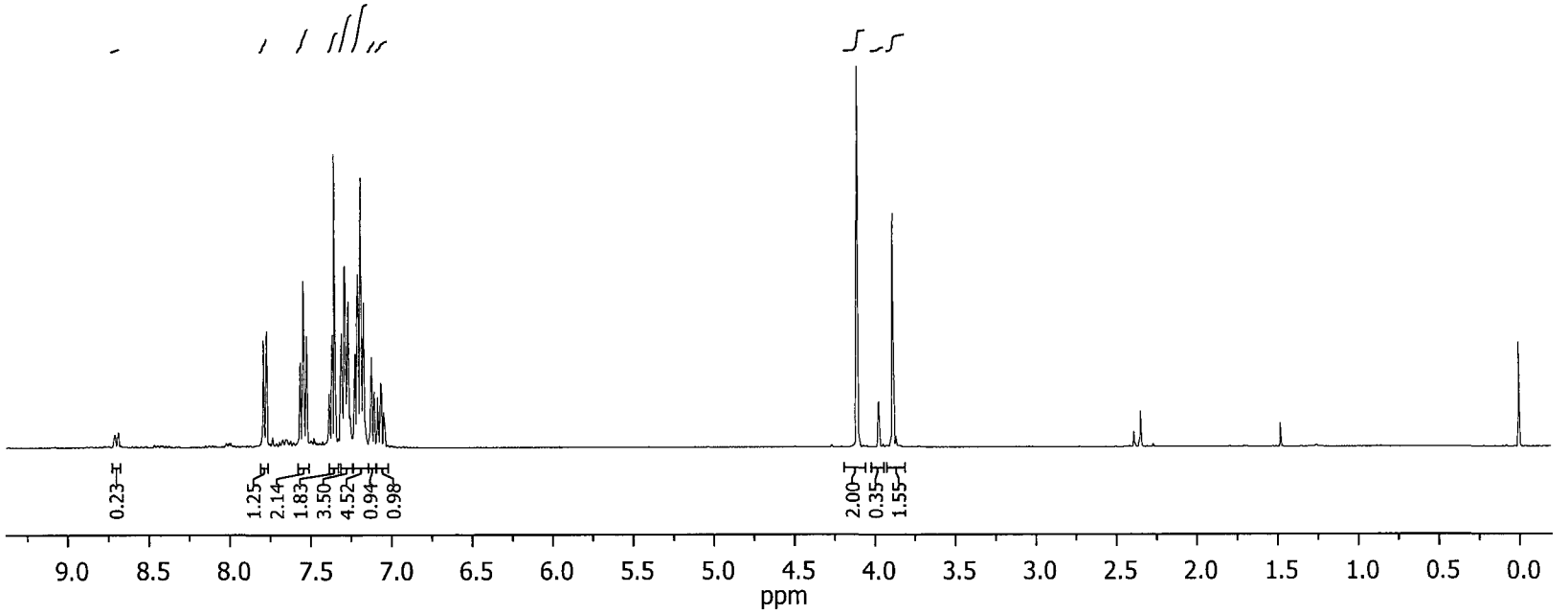
22


133.21
131.45
129.37
128.85
128.25
127.82
126.63
125.28
140.73
139.82
42.11
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


22
17
4.2
4.1
4.0
3.9
3.8
3.7
ppm
Br
22
FVP
800°C
0.06 torr
17
0.18
0.94
0.10
0.21
2.00
3.70
0.92
0.92
2.00
0.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


22
17
19
4.4
4.2
4.0
3.8
3.6
3.4
ppm


Br
MW/graphite
300°/300W
22
17
19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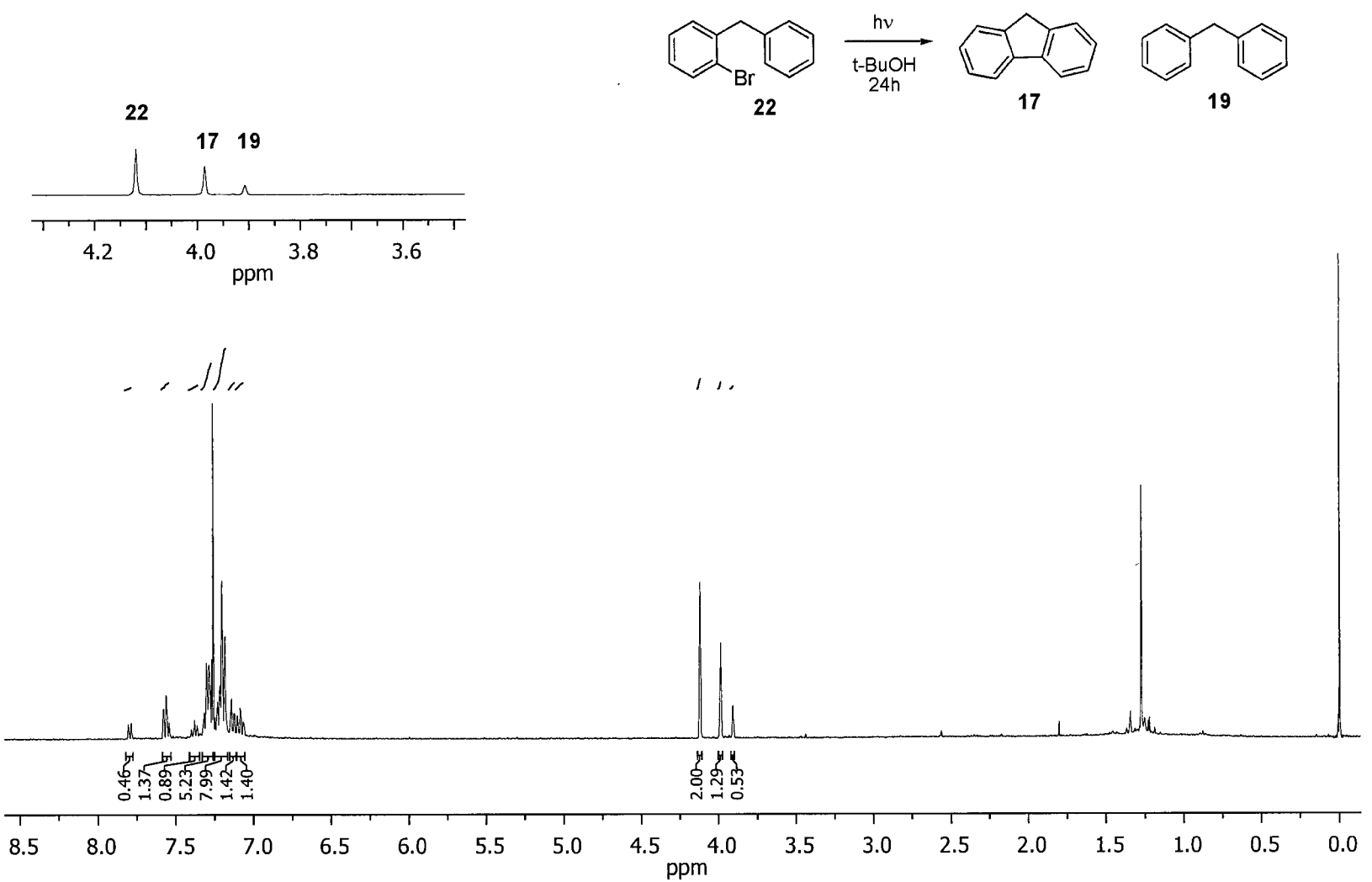
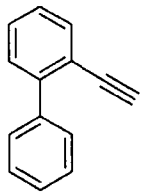
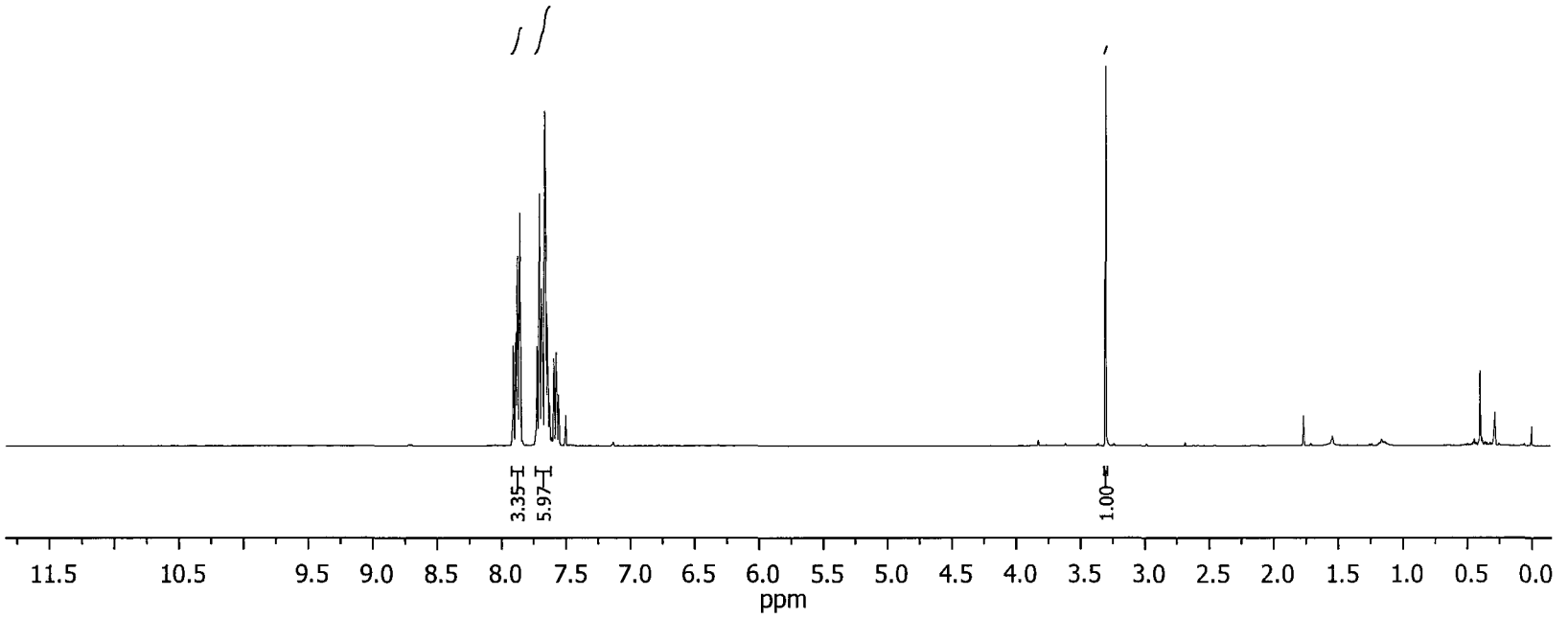
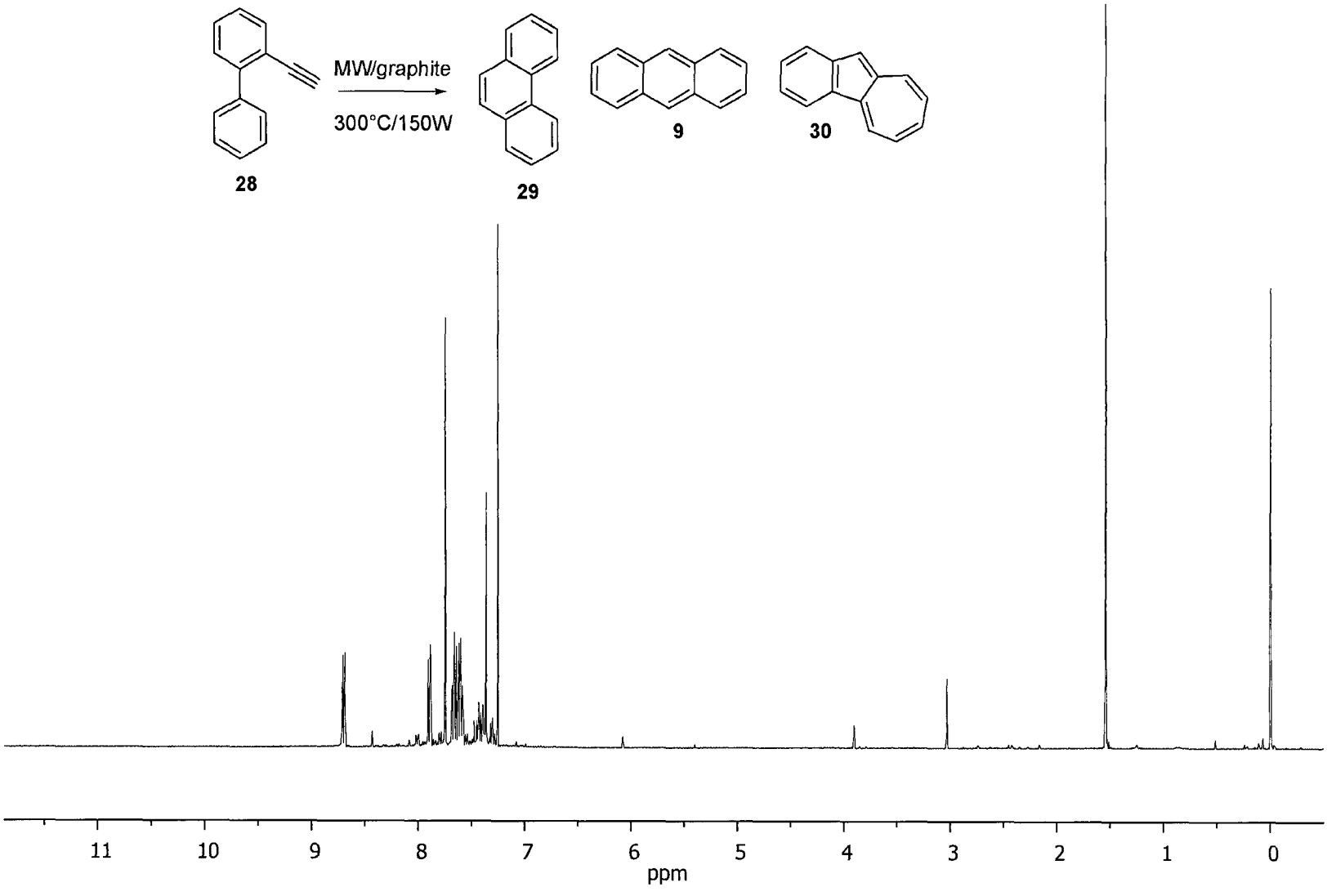
1.25
2.14
1.83
3.50
4.52
0.94
0.98
2.00
0.35
1.55
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

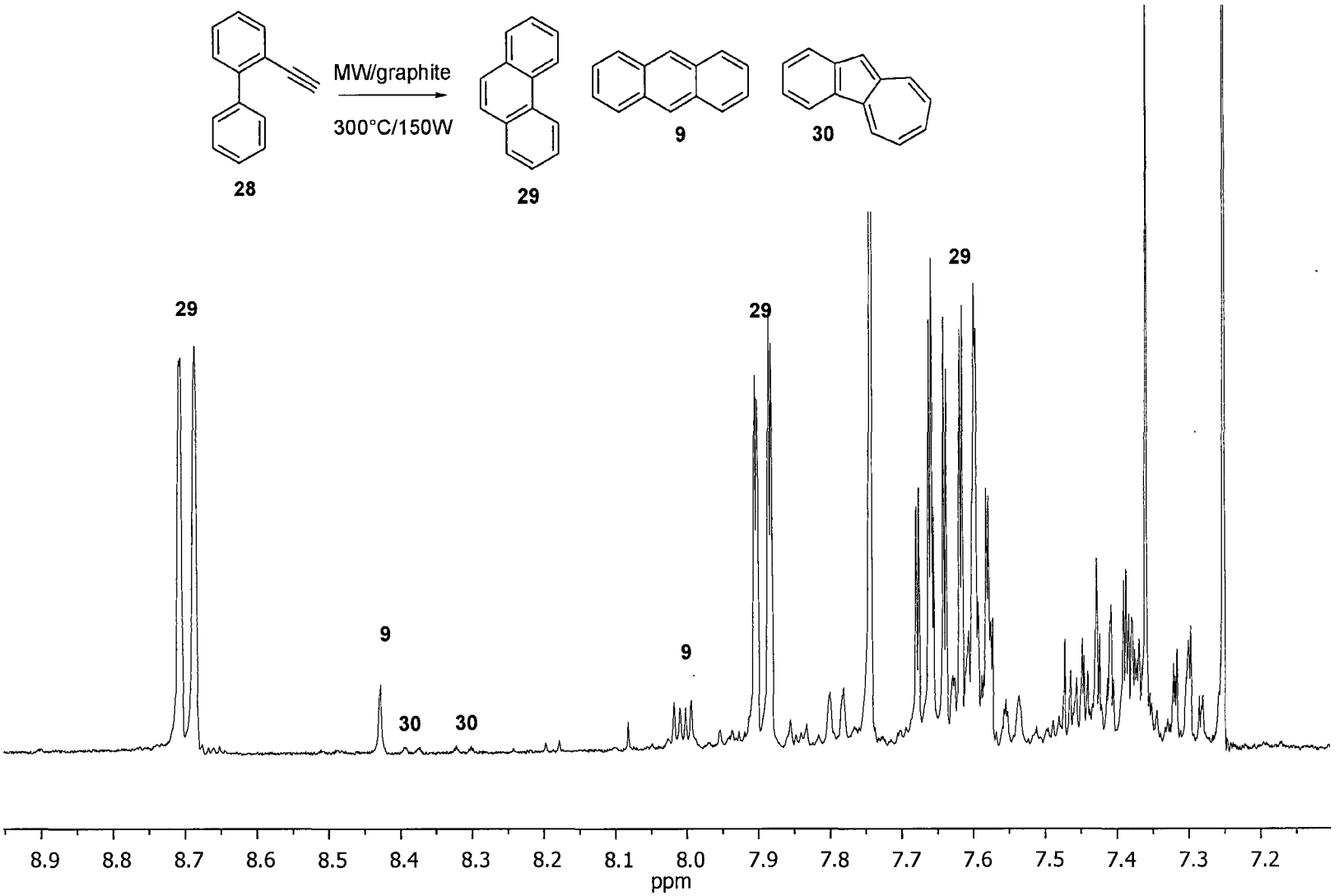

hν
t-BuOH
24h
Br
22
17
19
22
17 19
4.2
4.0
3.8
3.6
ppm
0.46
1.37
0.89
5.23
7.99
1.42
1.40
2.00
1.29
0.53
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

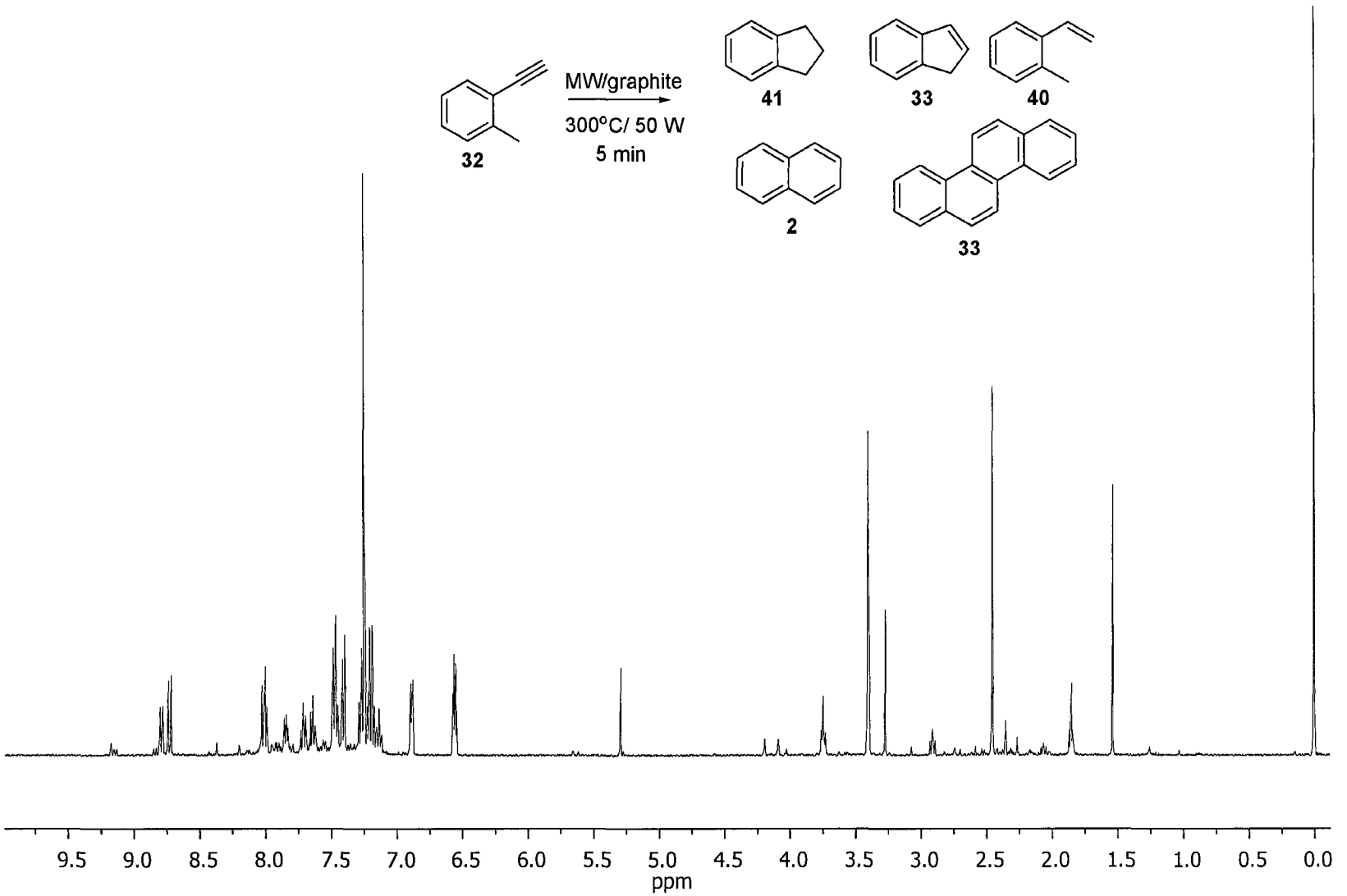


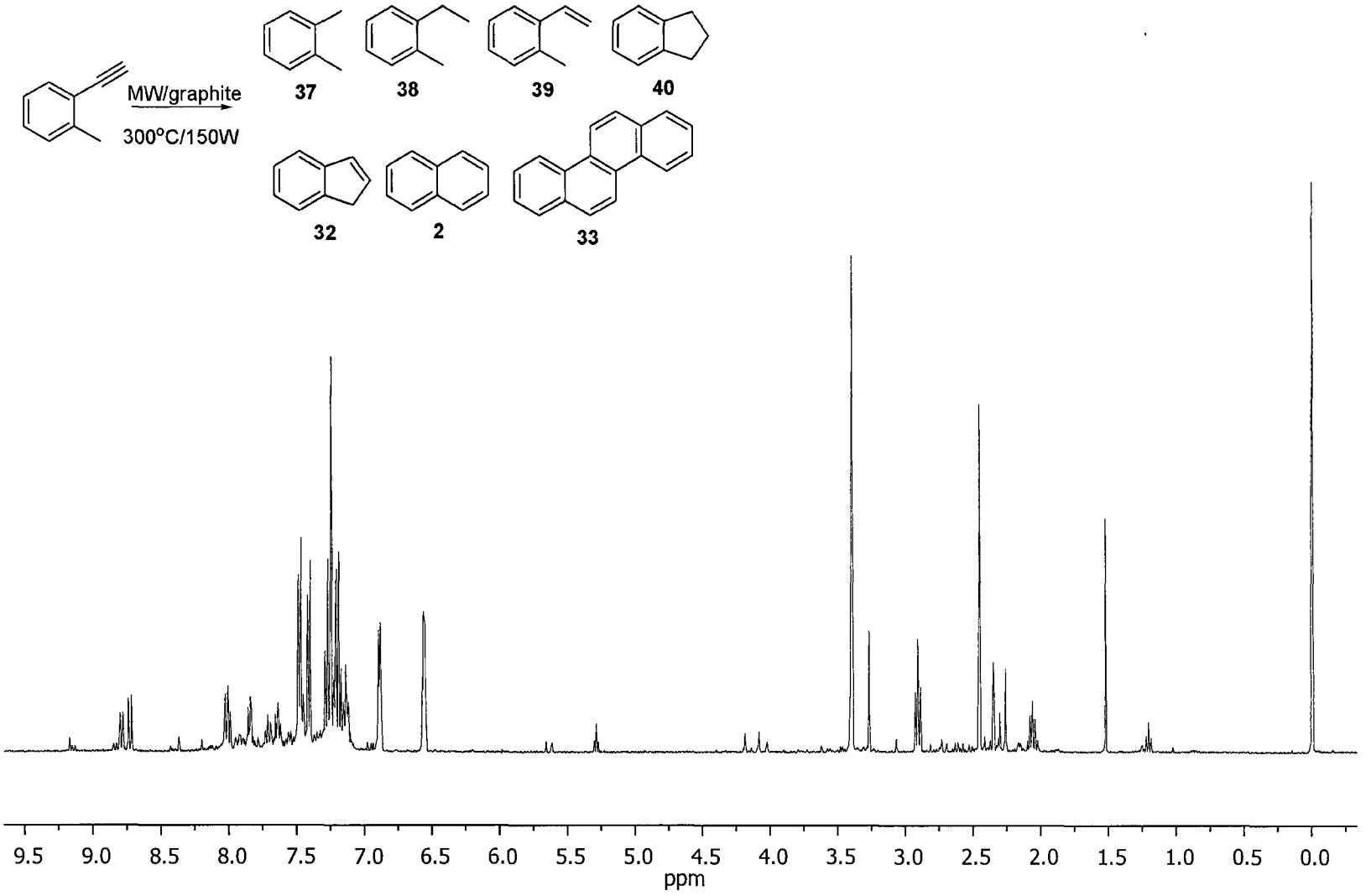
28

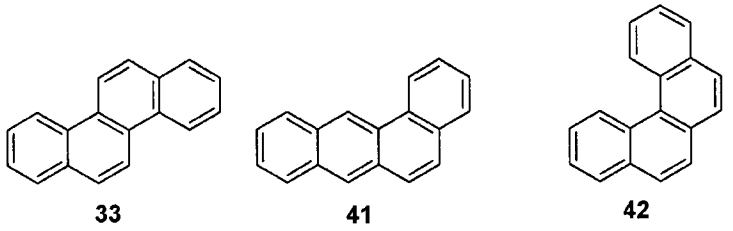

3.35
5.97
1.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

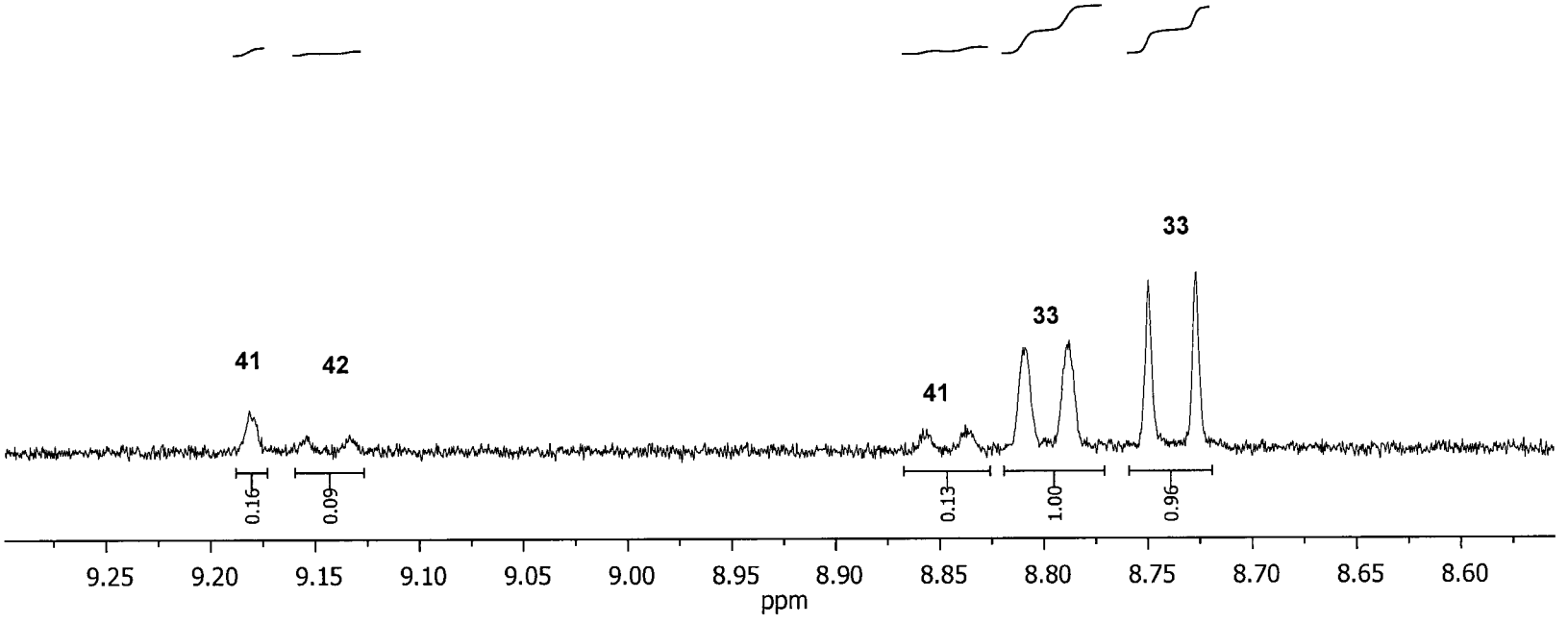

MW/graphite
300°C/150W
28
29
9
30
11
10
9
8
7
6
5
4
3
2
1
0
ppm

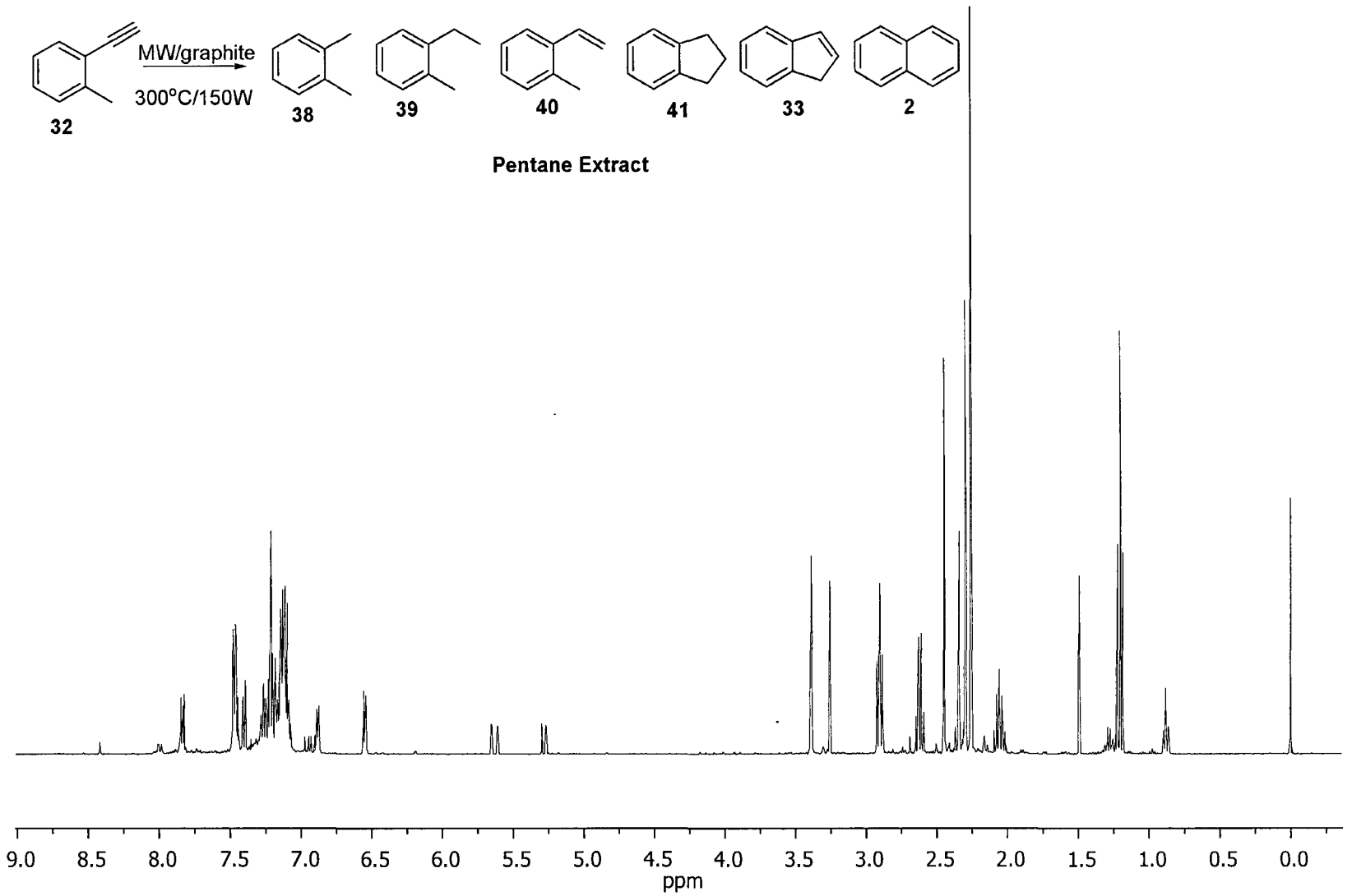

MW/graphite
300°C/150W
28
29
9
30
29
29
29
9
9
30
30
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm

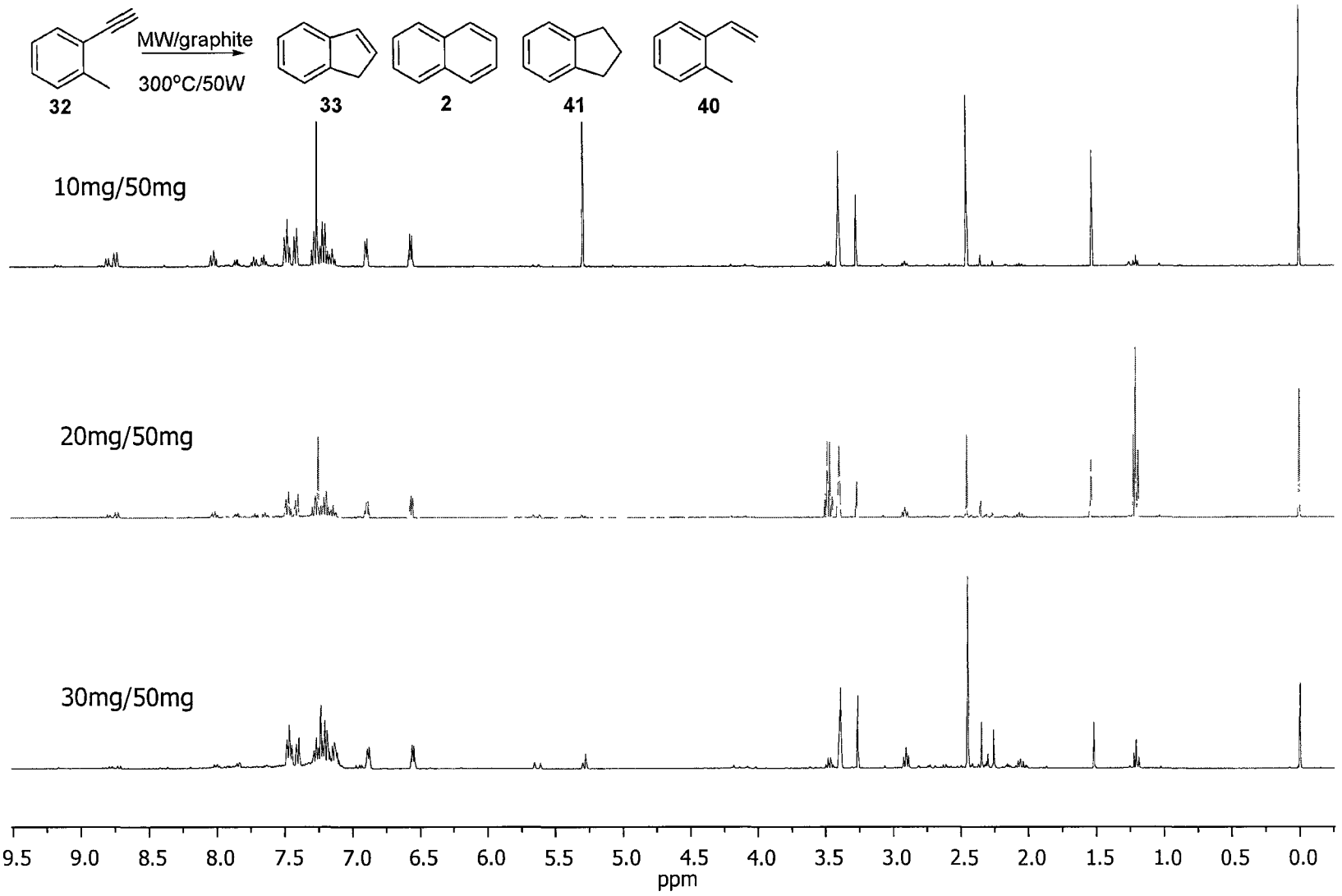

MW/graphite
300°C/ 50 W
5 min
32
41
33
40
2
33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

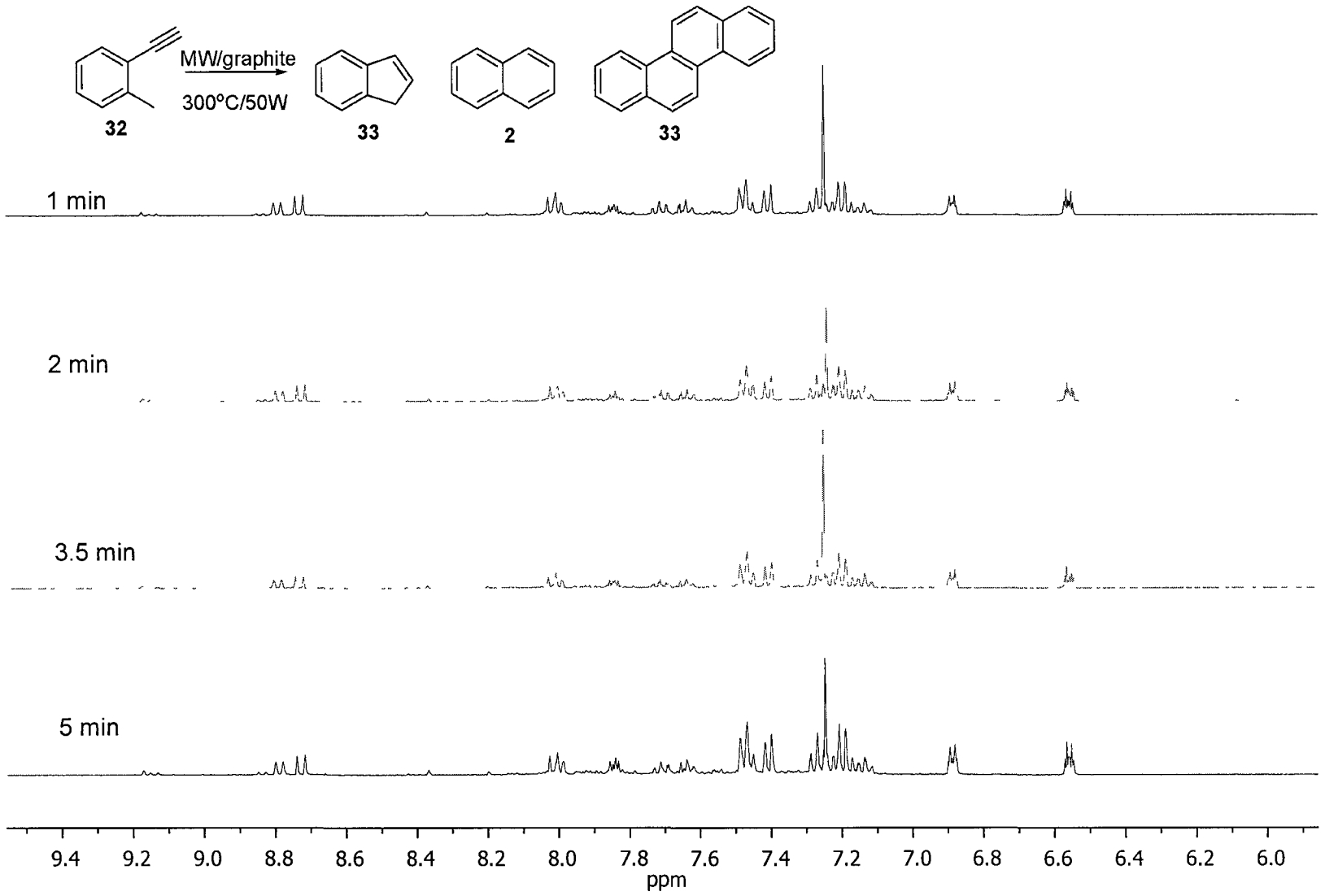

MW/graphite
300°C/150W
37
38
39
40
32
2
33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

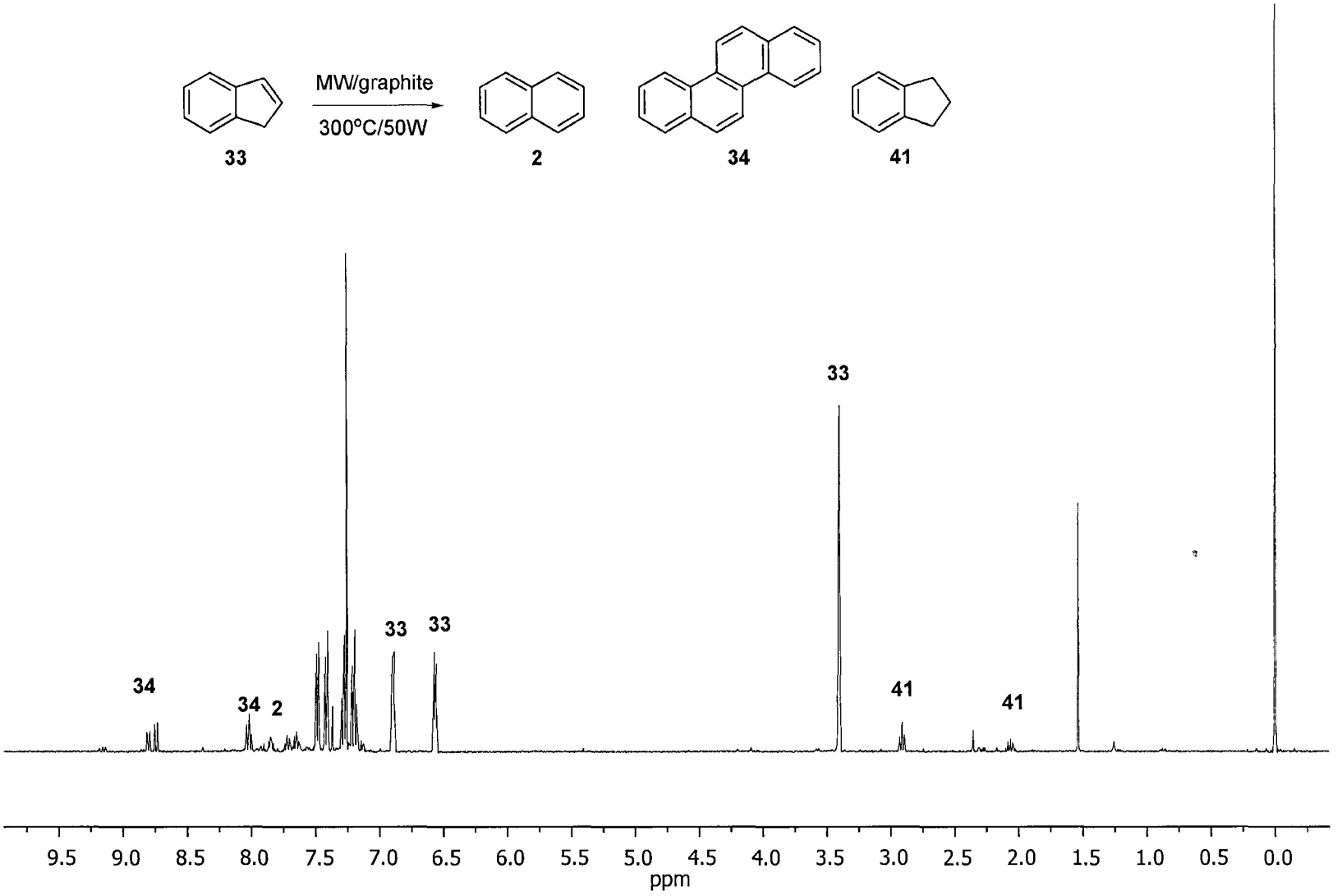

33
41
42
71:23:6

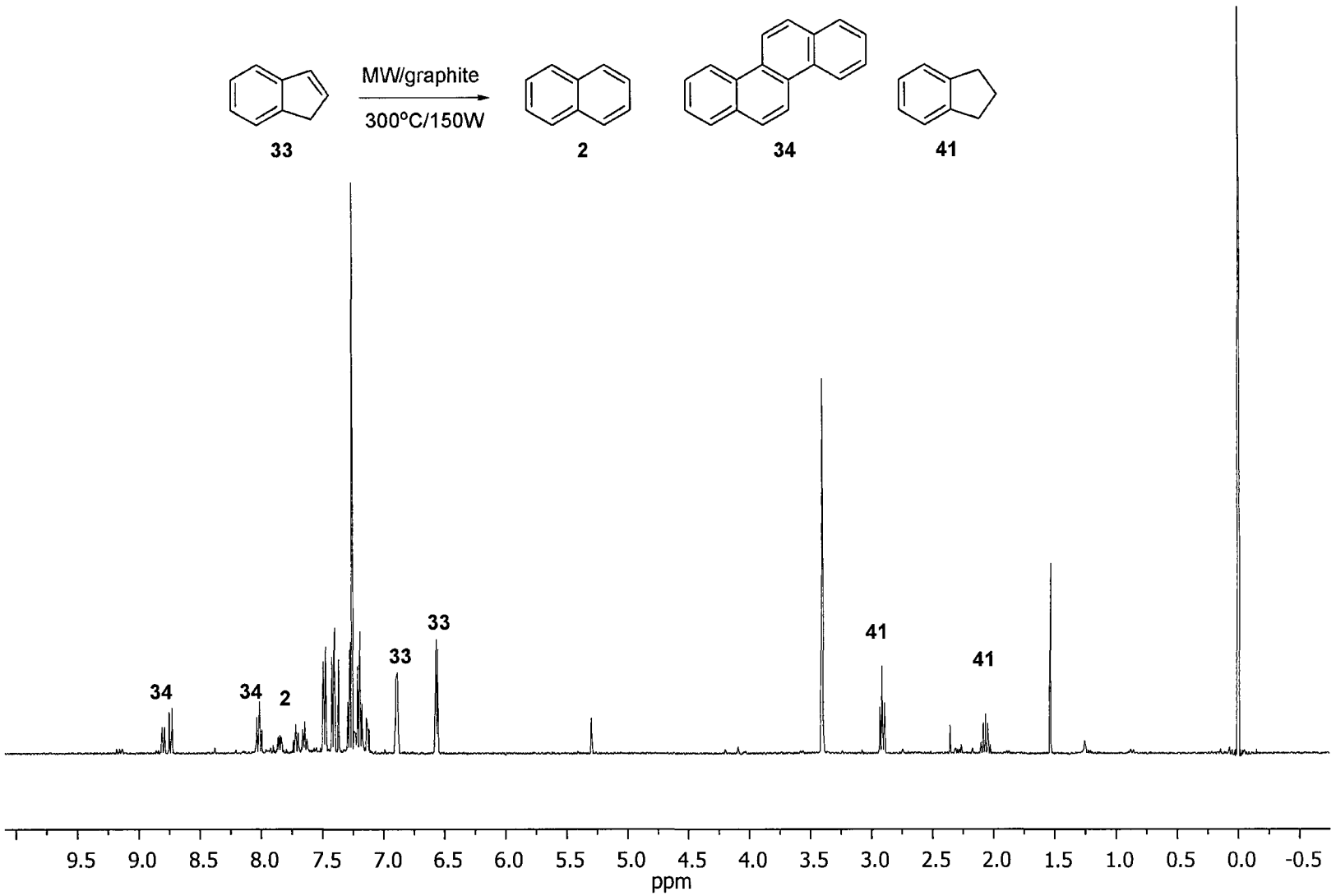

41
42
41
33
33
0.16
0.09
0.13
1.00
0.96
9.25
9.20
9.15
9.10
9.05
9.00
8.95
8.90
8.85
8.80
8.75
8.70
8.65
8.60
ppm

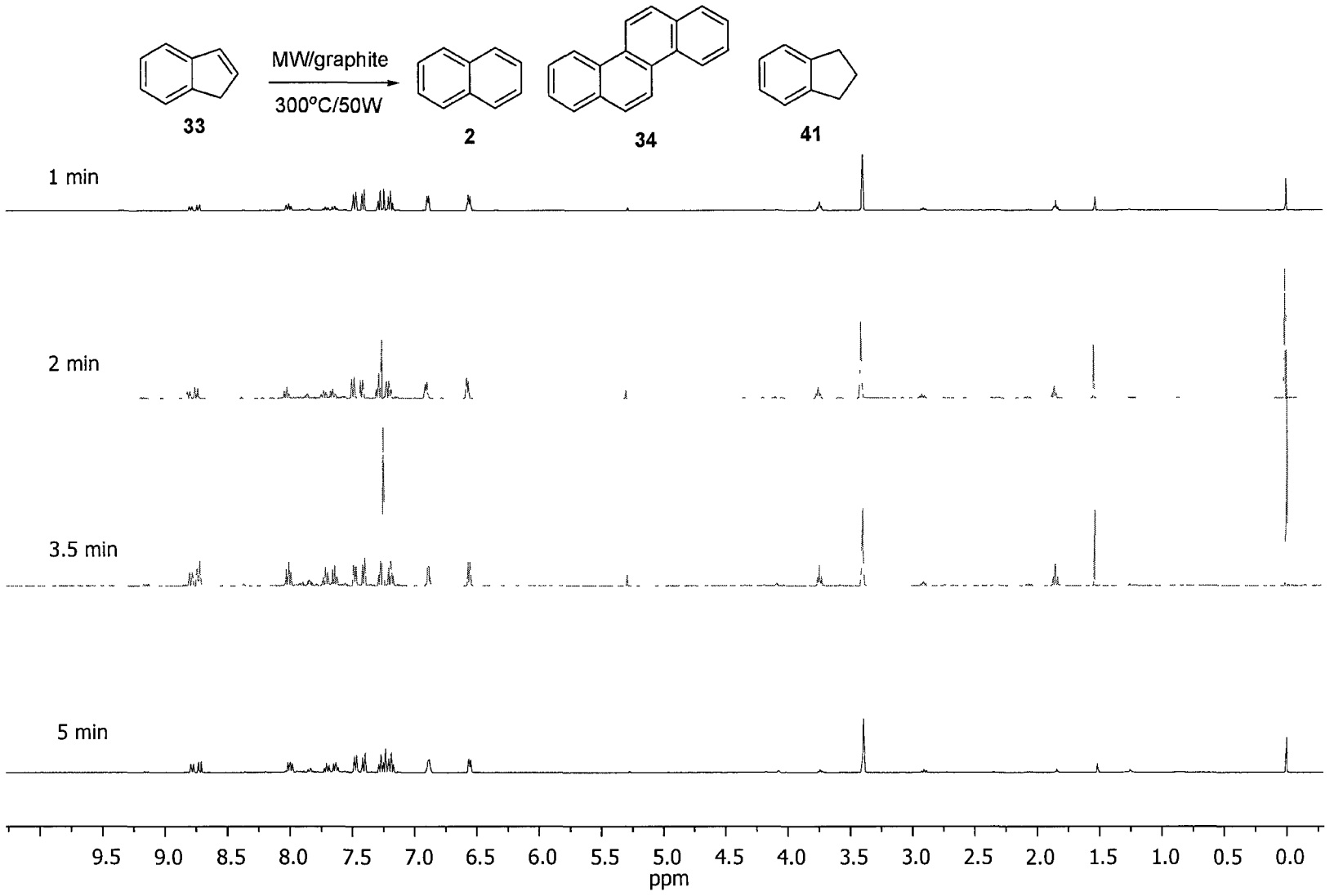

MW/graphite
300°C/150W
32
38
39
40
41
33
2
Pentane Extract
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

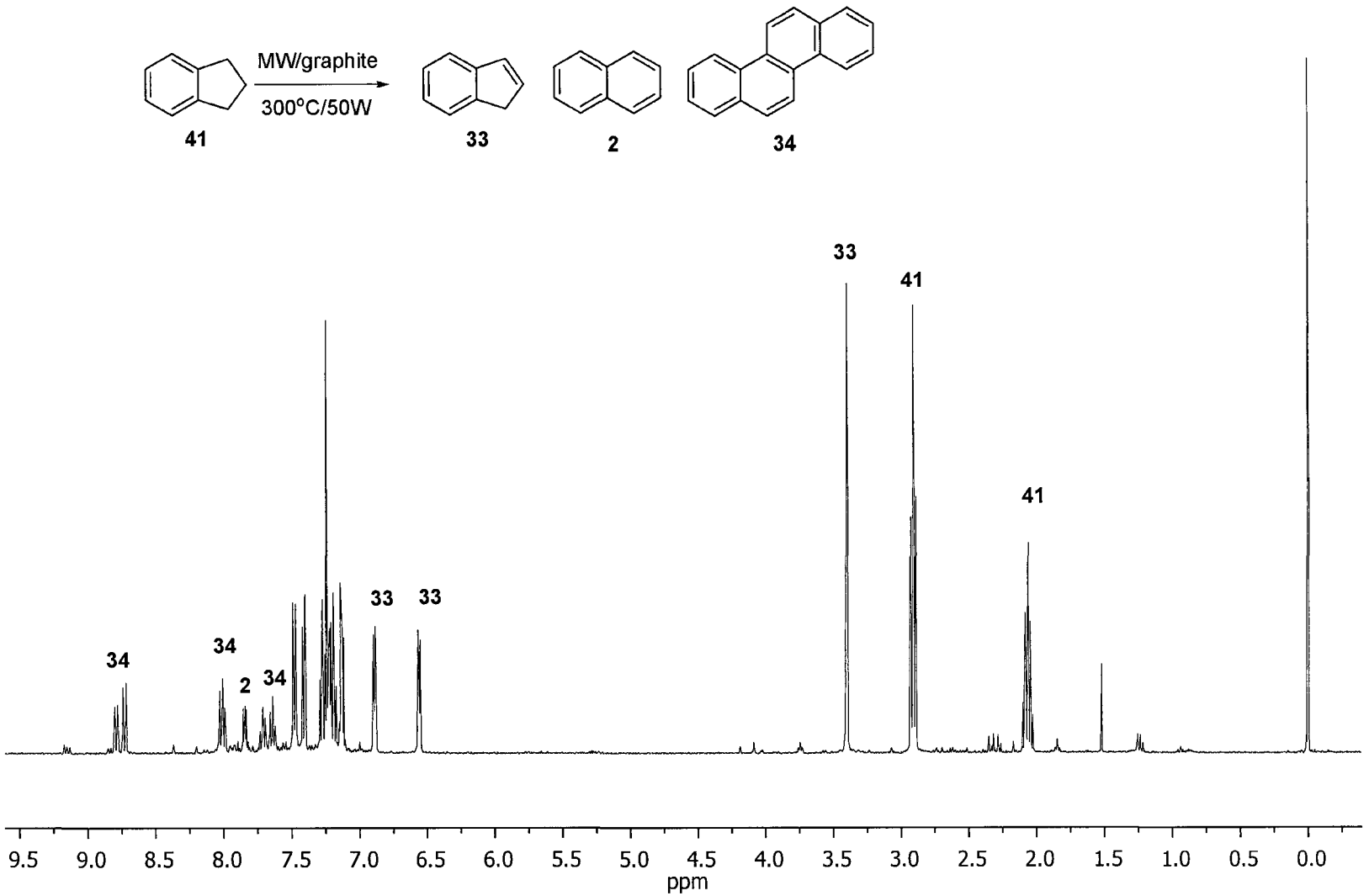

MW/graphite
300°C/50W
32
33
2
41
40
10mg/50mg
20mg/50mg
30mg/50mg
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

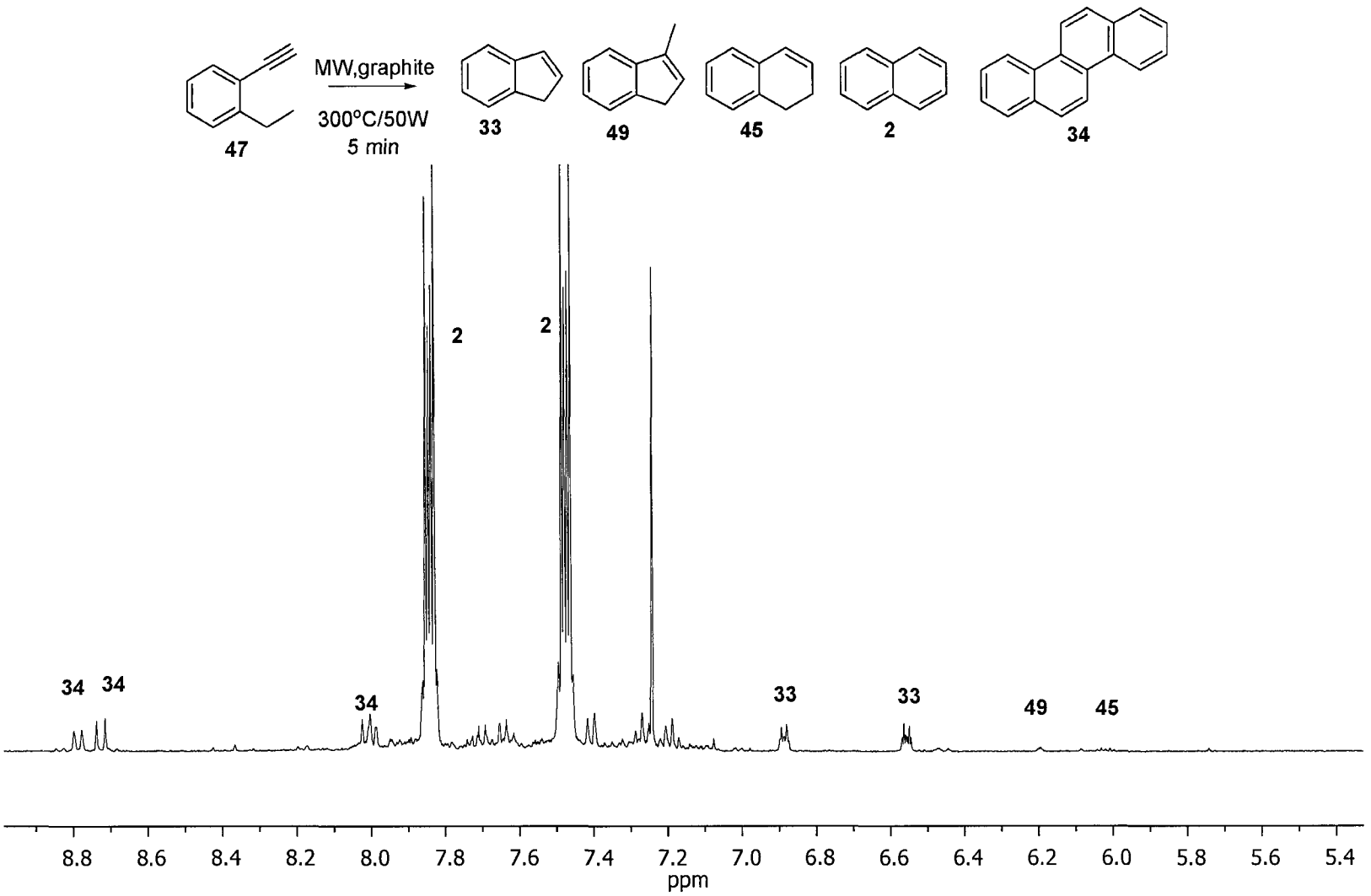

MW/graphite
300°C/50W
32
33
2
33
1 min
2 min
3.5 min
5 min
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
ppm

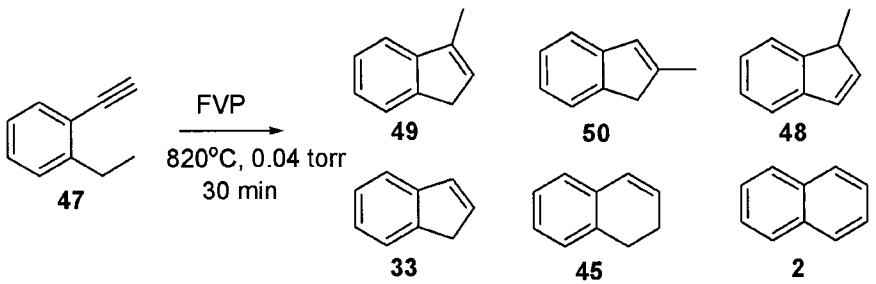

MW/graphite
300°C/50W
33
2
34
41
34
34
2
33
33
33
41
41
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

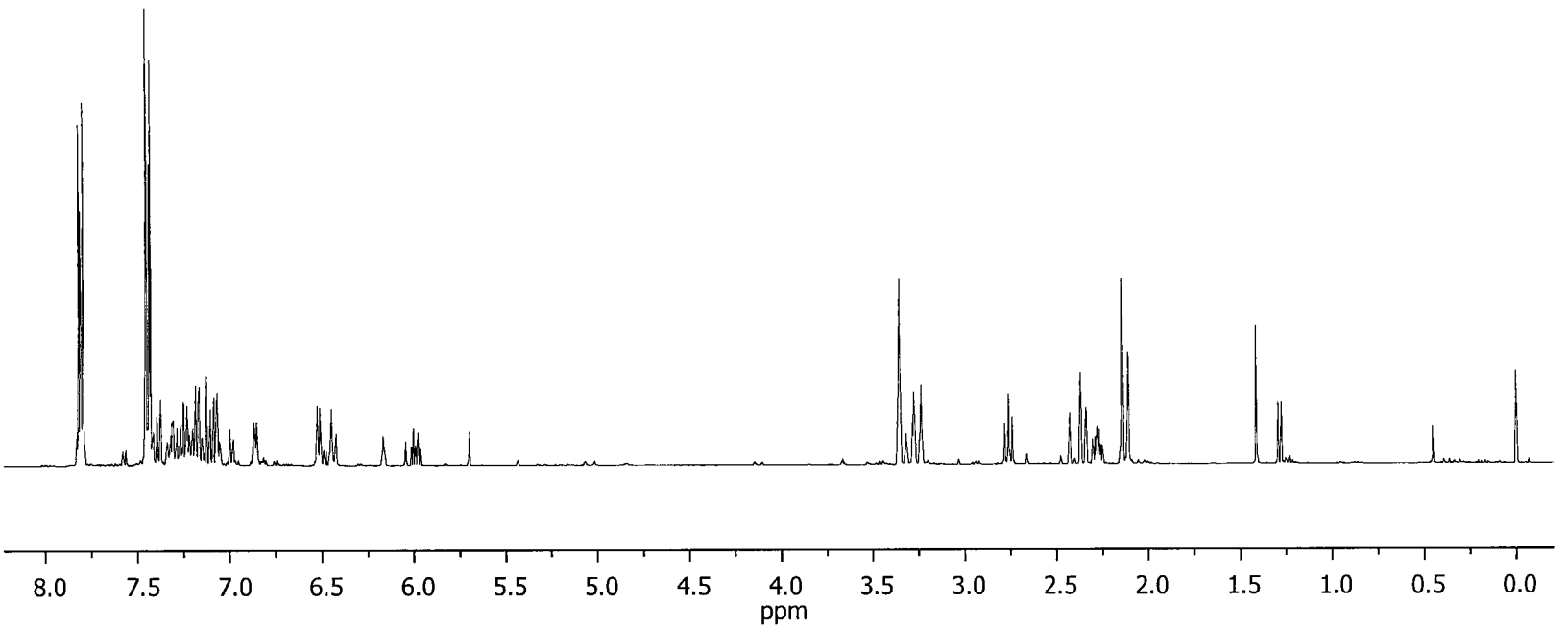

MW/graphite
300°C/150W
33
2
34
41
34
34
2
33
33
41
41
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

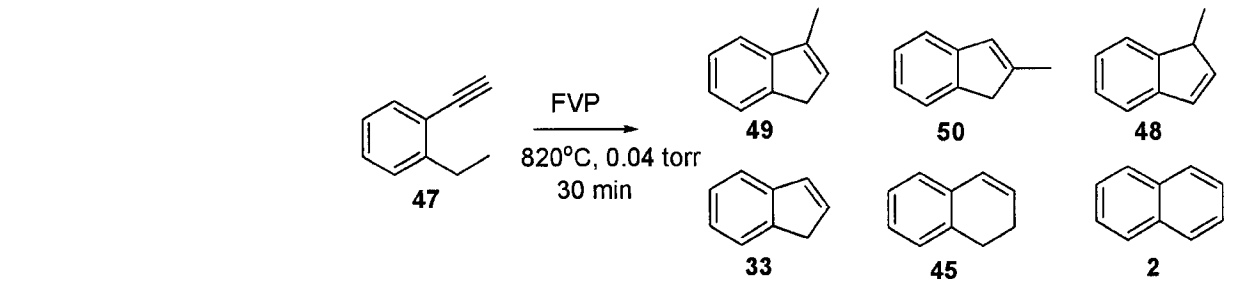

MW/graphite
300°C/50W
33
2
34
41
1 min
2 min
3.5 min
5 min
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

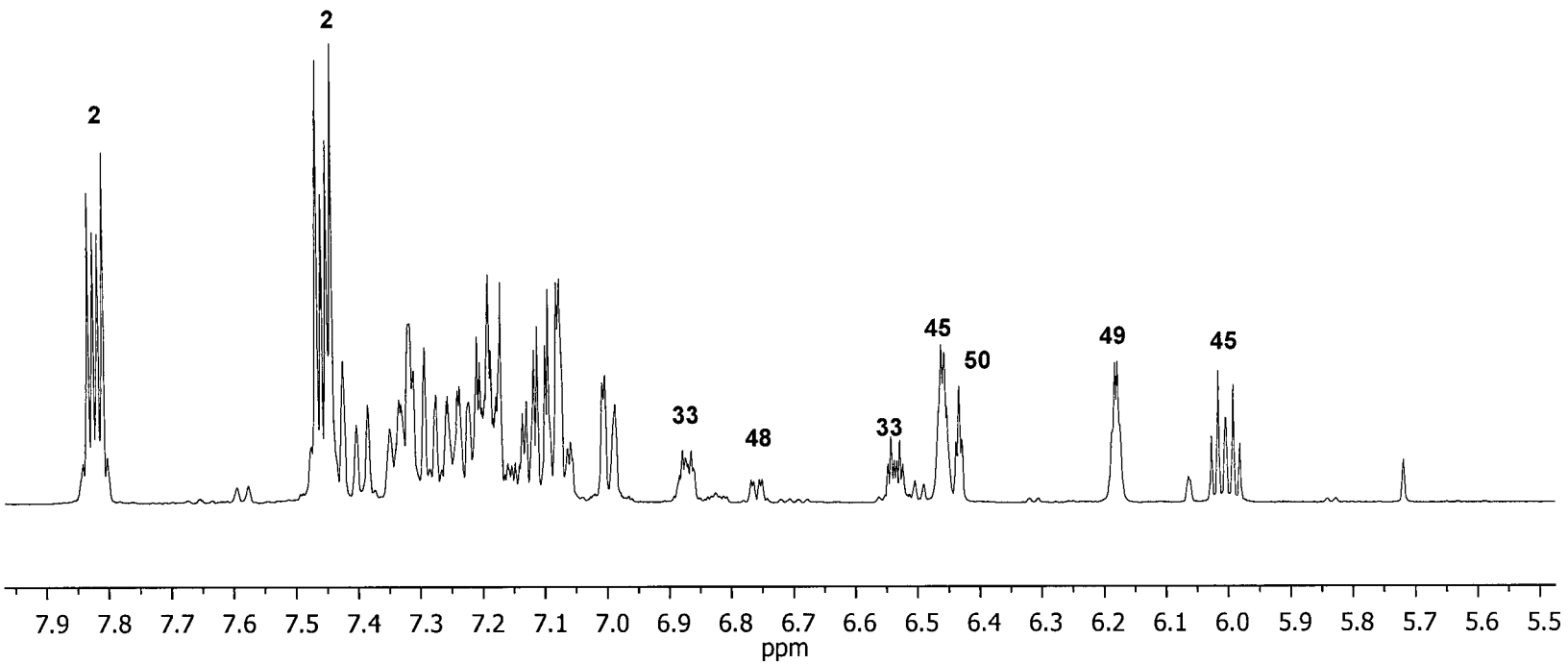

MW/graphite
300°C/50W
41
33
2
34
33
41
41
34
34
2
34
33
33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

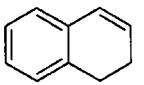

MW,graphite
300°C/50W
5 min
47
33
49
45
2
34
34
34
34
2
2
33
33
49
45
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
ppm


FVP
820°C, 0.04 torr
30 min
47
49
50
48
33
45
2

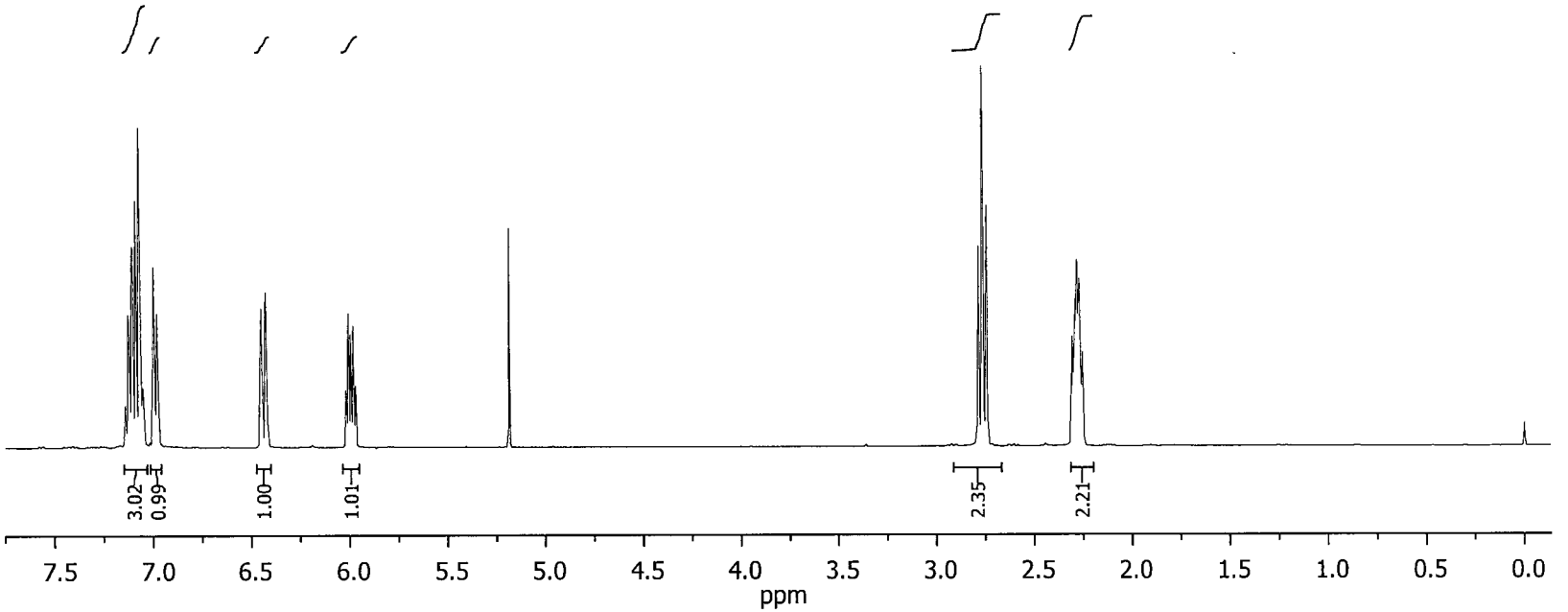

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

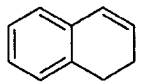

FVP
820°C, 0.04 torr
30 min
47
49
50
48
33
45
2


2
2
33
48
33
45
50
49
45
7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5
ppm

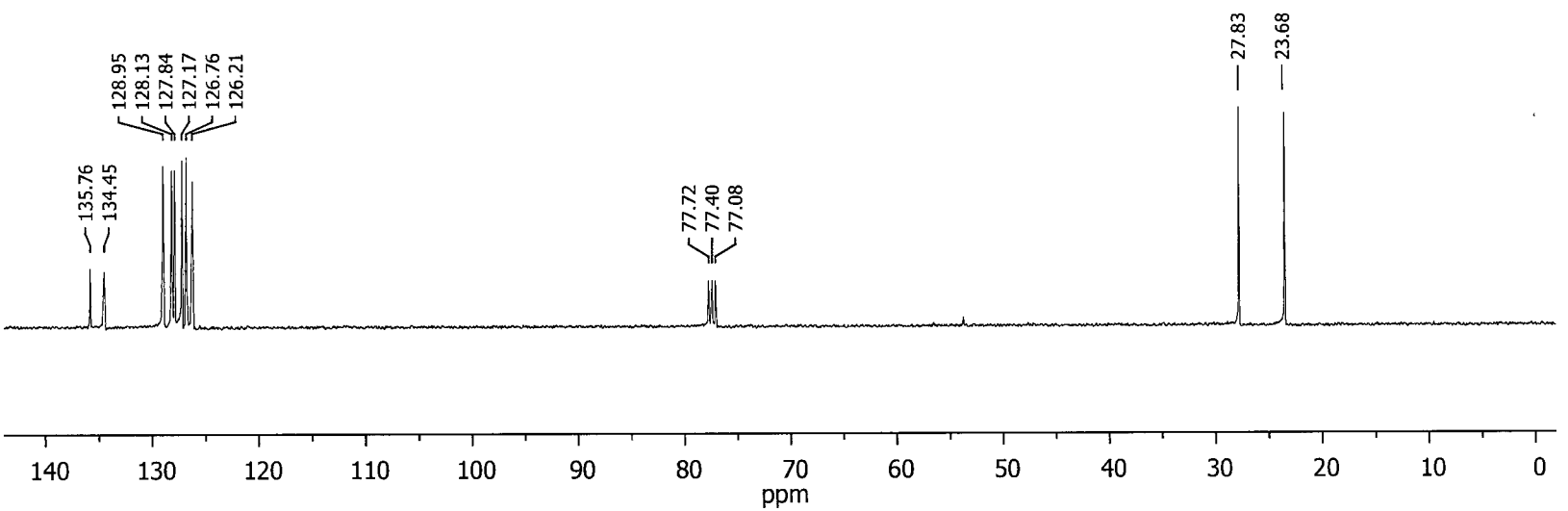


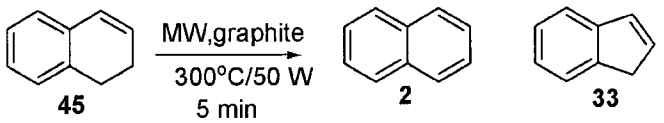
45

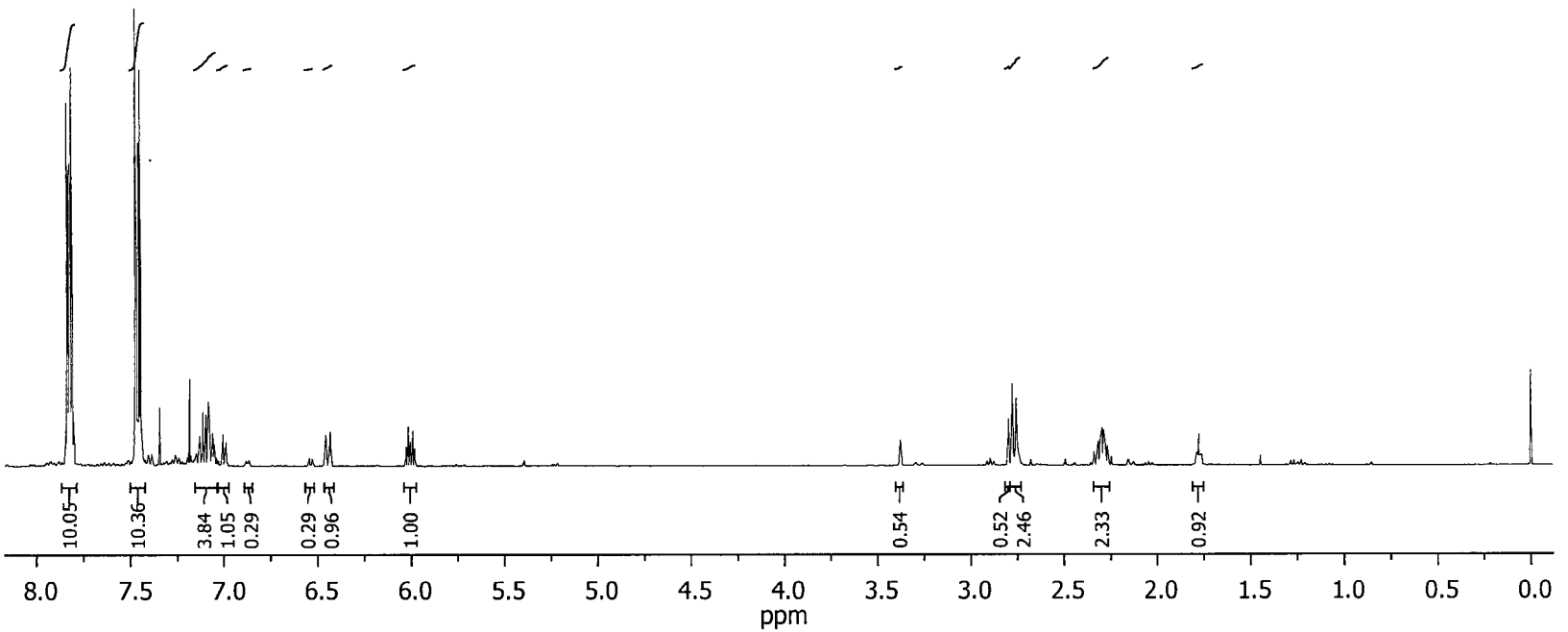

3.02
0.99
1.00
1.01
2.35
2.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

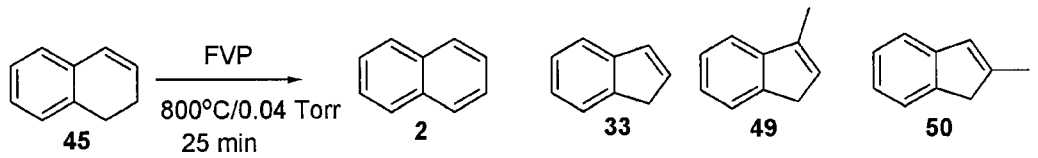


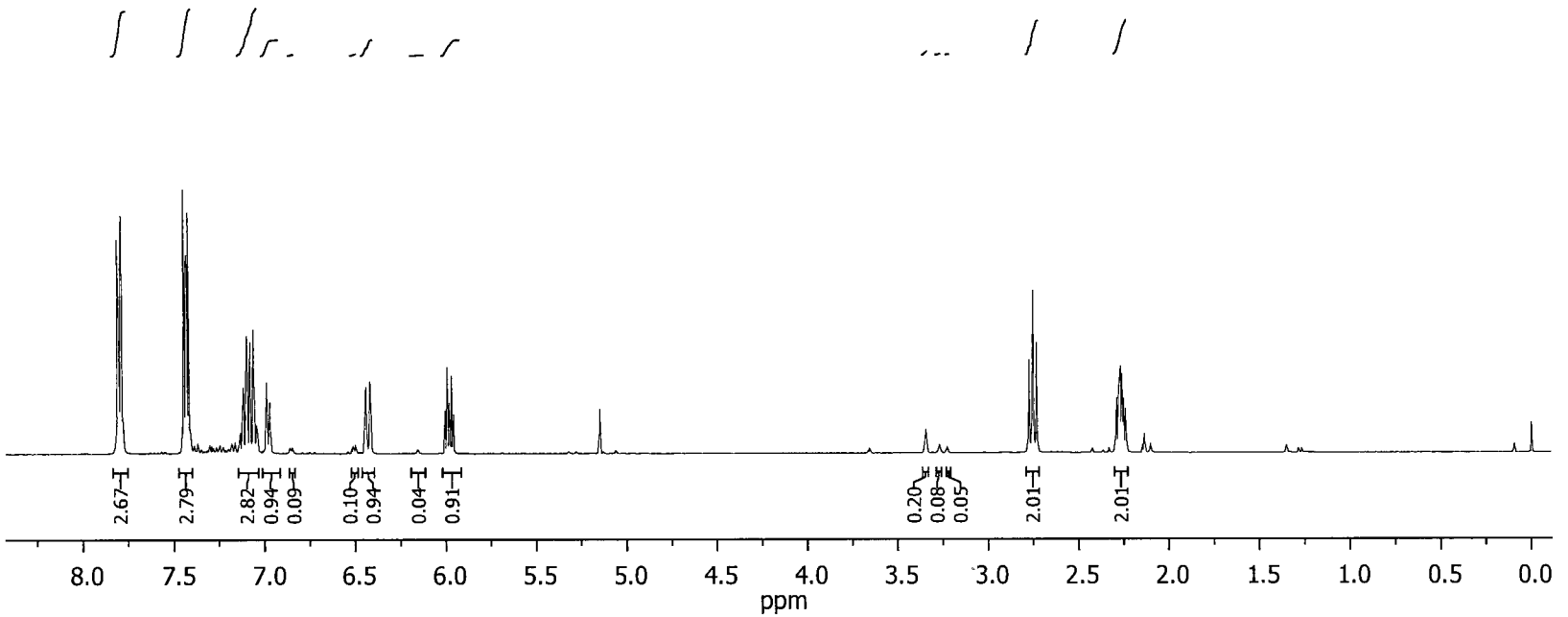
45

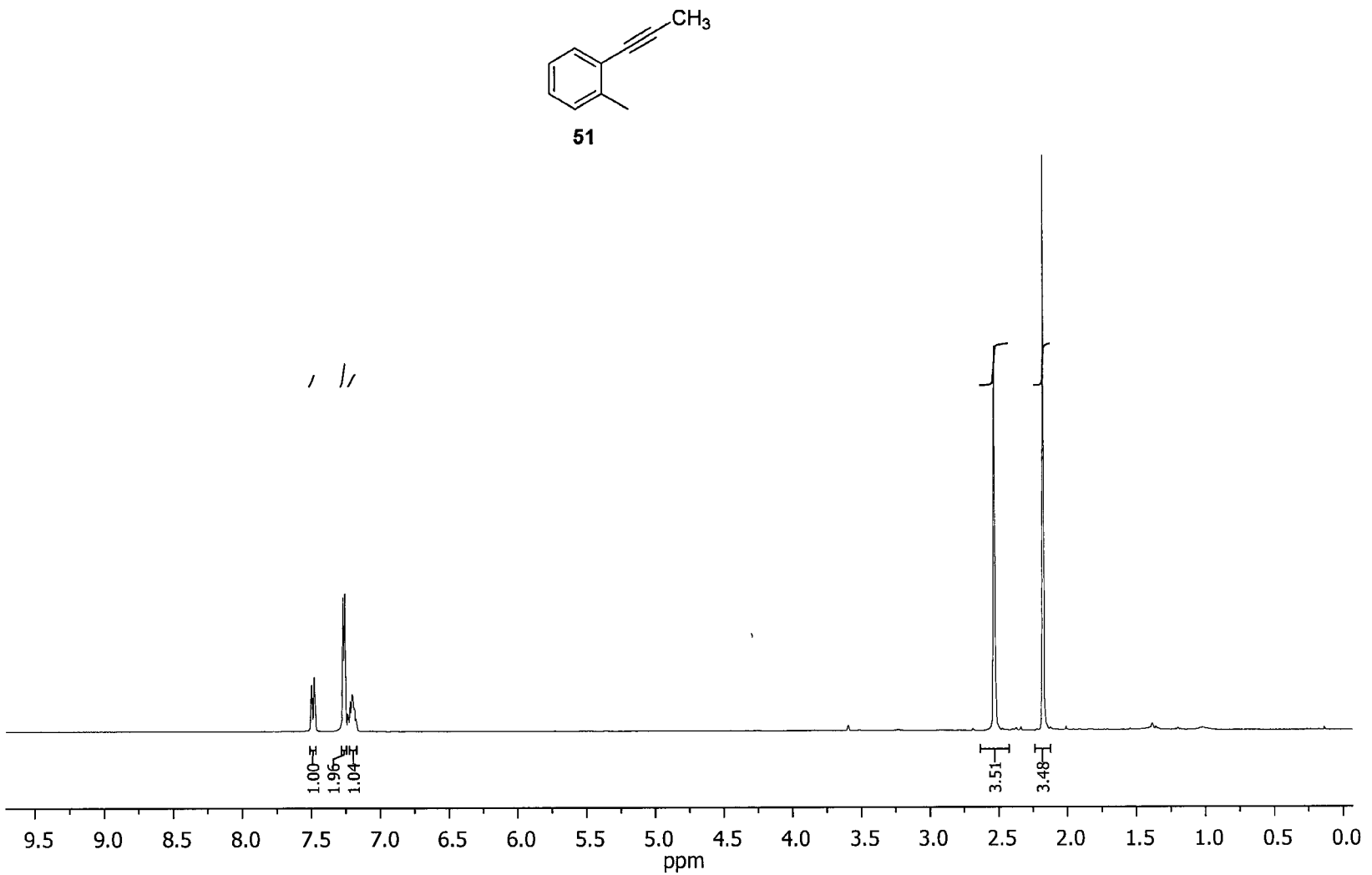

135.76
134.45
128.95
128.13
127.84
127.17
126.76
126.21
77.72
77.40
77.08
27.83
23.68
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

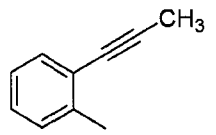

MW,graphite
300°C/50 W
5 min
45
2
33


10.05
10.36
3.84
1.05
0.29
0.29
0.96
1.00
0.54
0.52
2.46
2.33
0.92
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

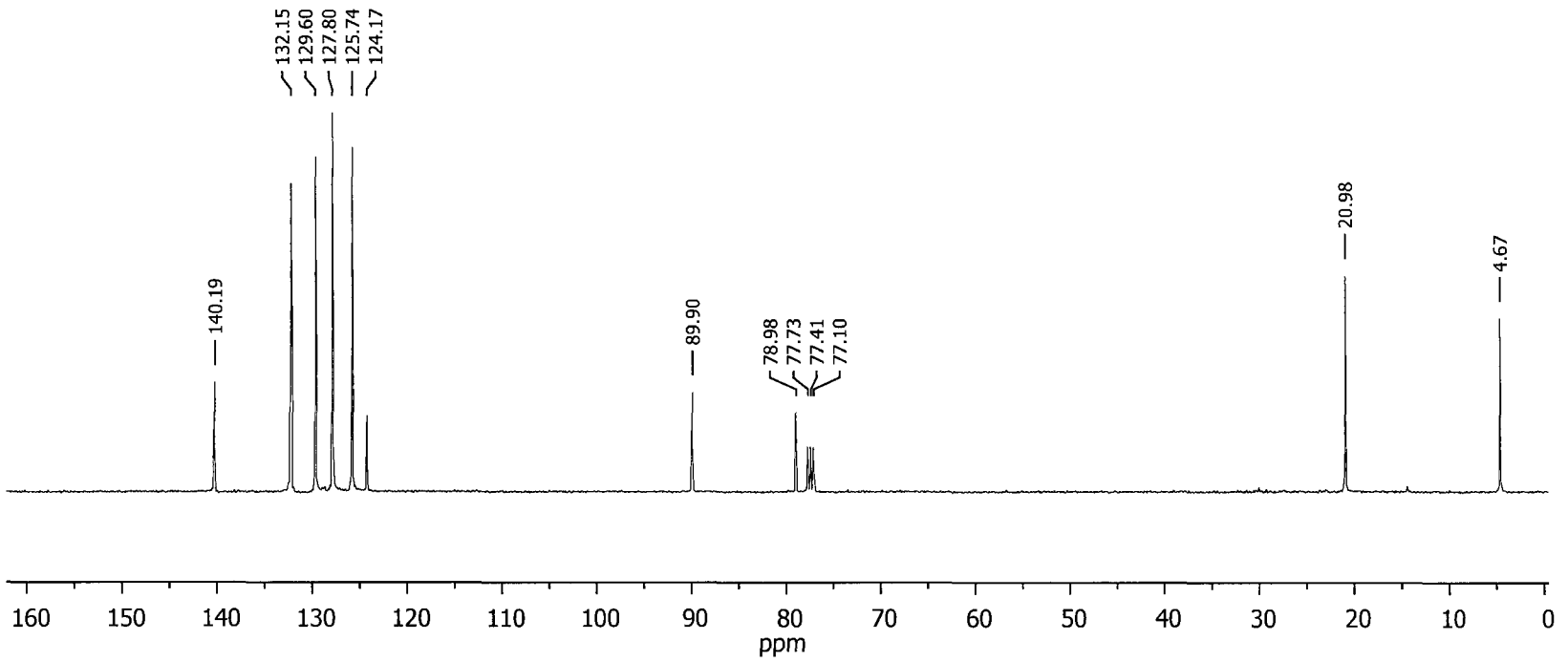

FVP
800°C/0.04 Torr
25 min
45
2
33
49
50

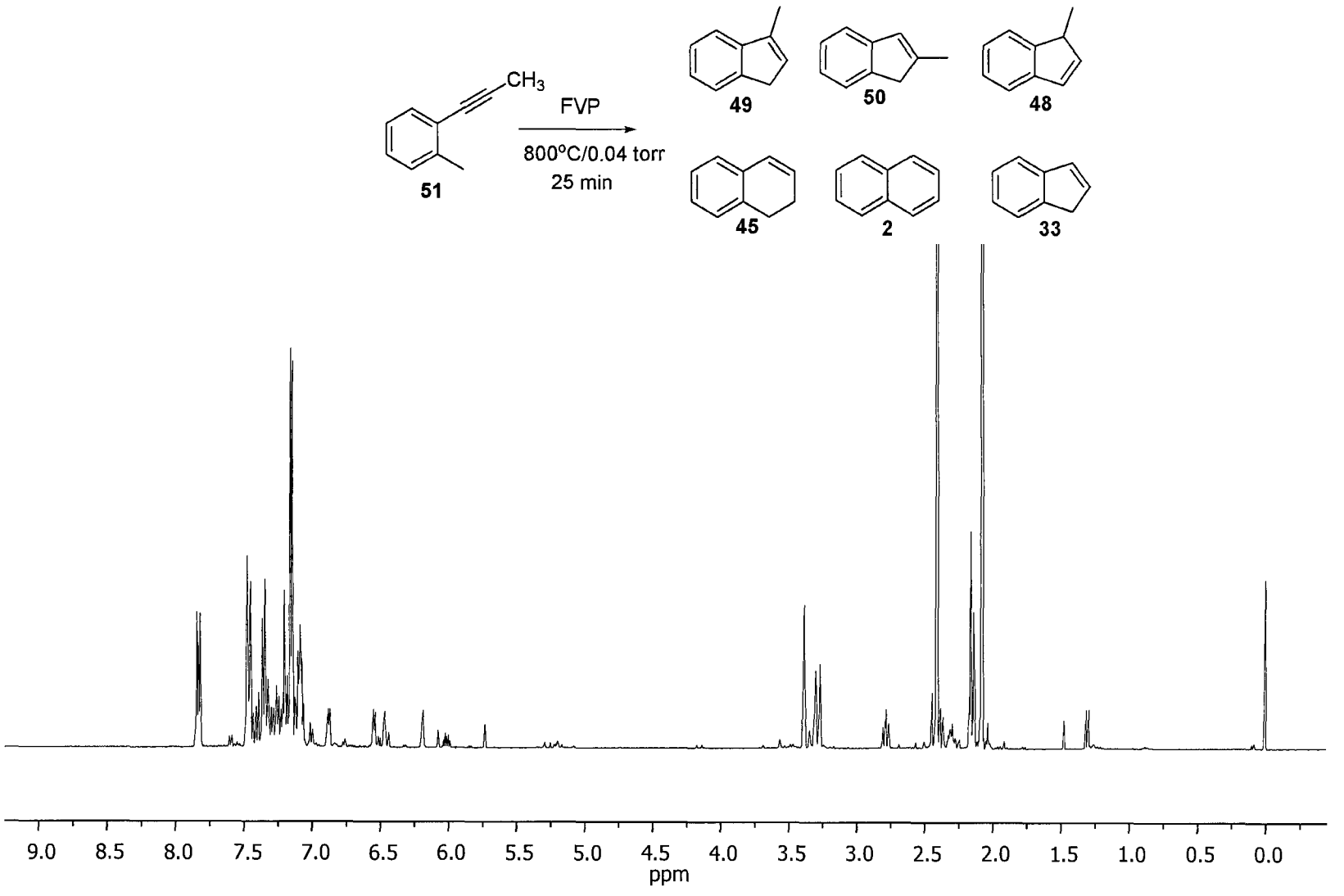

2.67
2.79
2.82
0.94
0.09
0.10
0.94
0.04
0.91
0.20
0.08
0.05
2.01
2.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

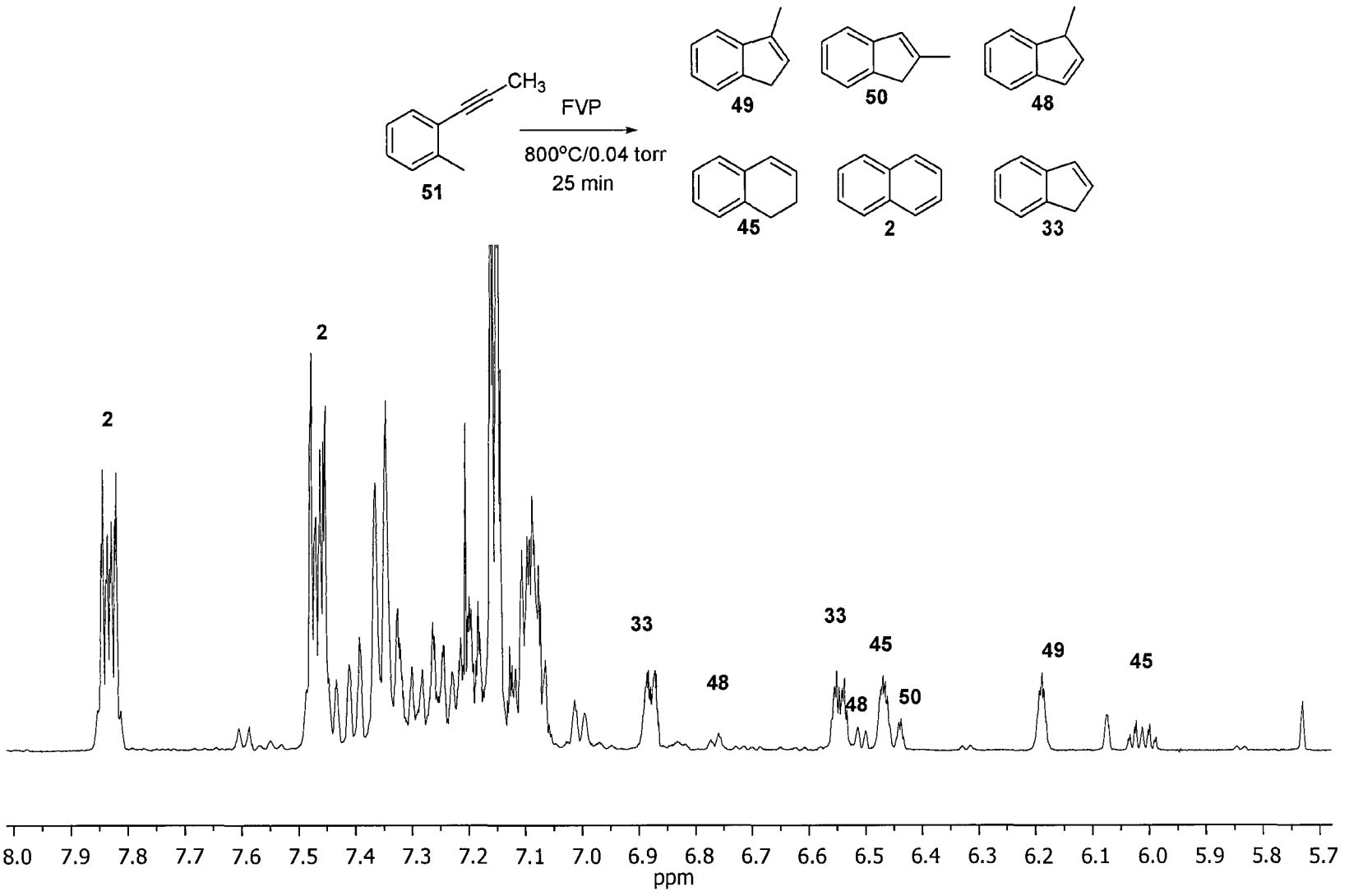

CH3
51
1.00
1.96
1.04
3.51
3.48
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

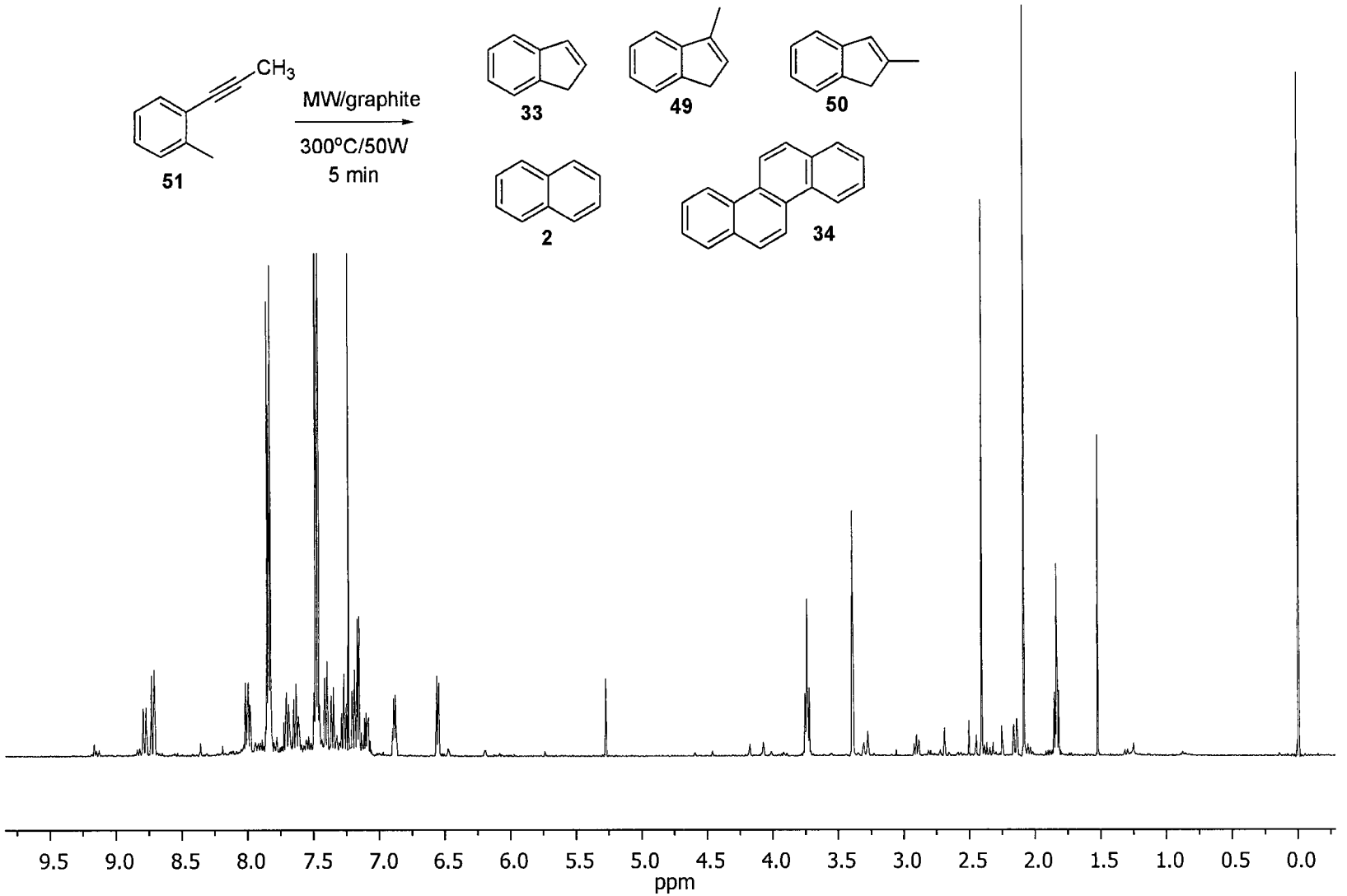

CH3

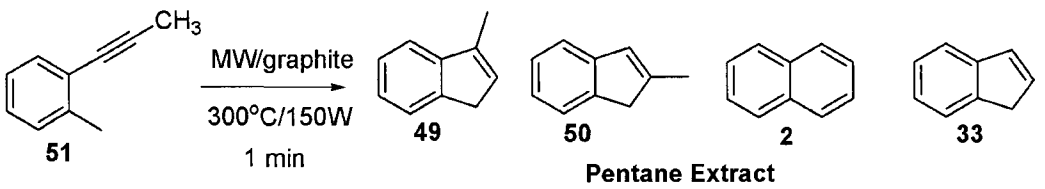
51

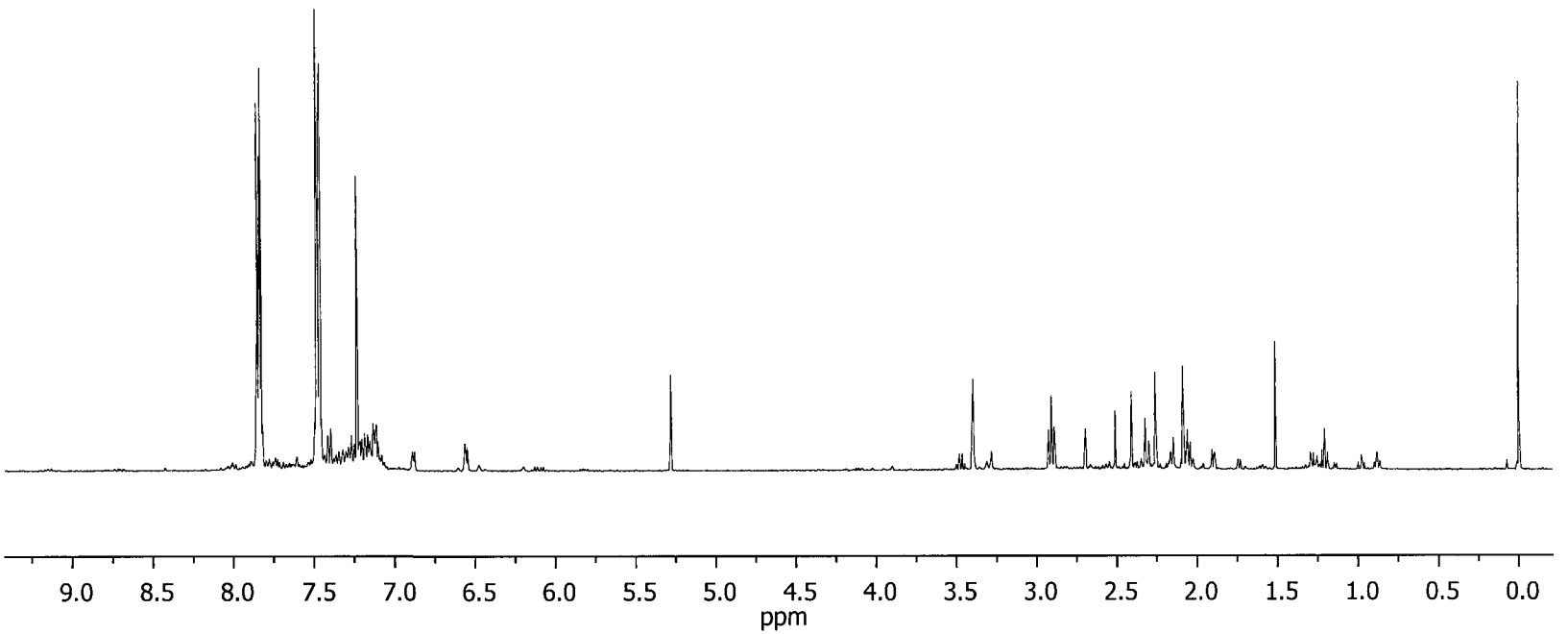

132.15
129.60
127.80
125.74
124.17
140.19
89.90
78.98
77.73
77.41
77.10
20.98
4.67
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

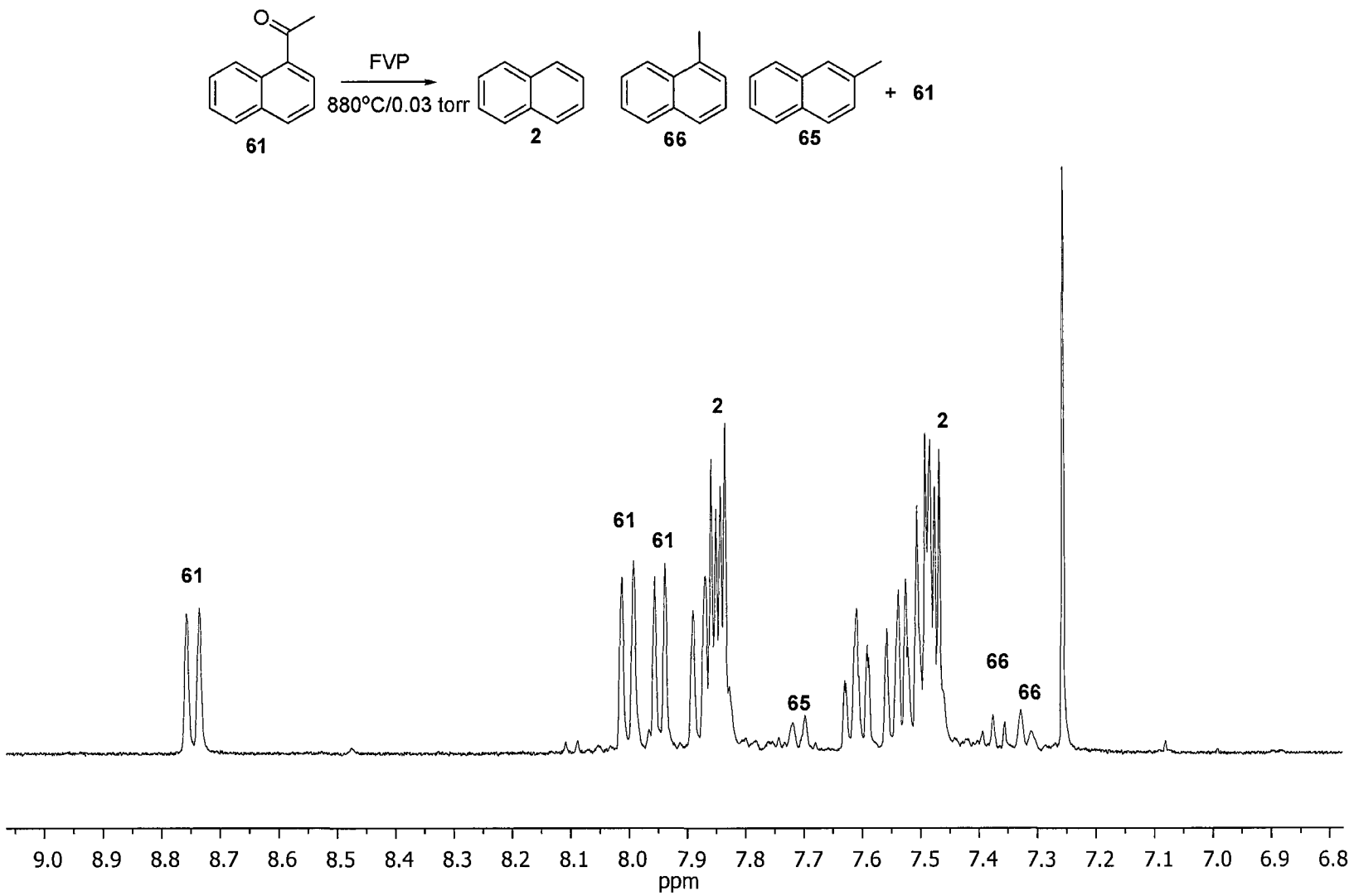

CH3
FVP
800°C/0.04 torr
25 min
51
49
50
48
45
2
33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

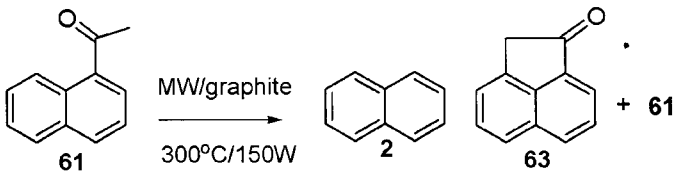

CH3
FVP
800°C/0.04 torr
25 min
51
49
50
48
45
2
33
2
2
33
48
33
48
45
50
49
45
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7
ppm

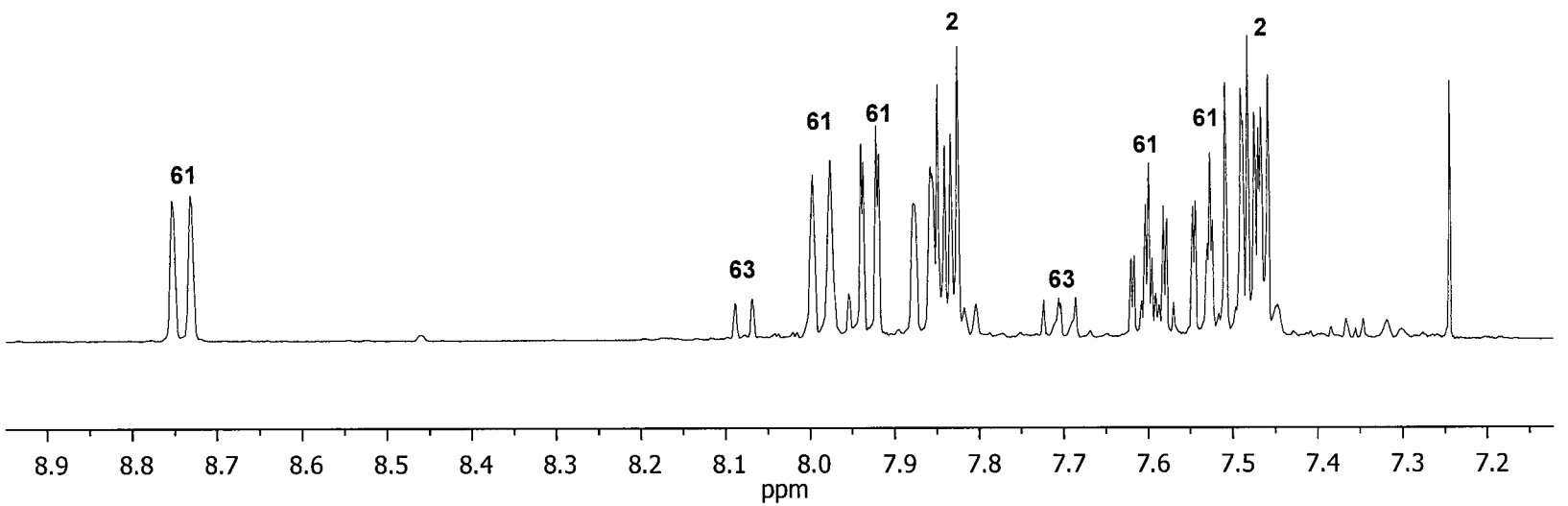

CH3
MW/graphite
300°C/50W
5 min
51
33
49
50
2
34
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

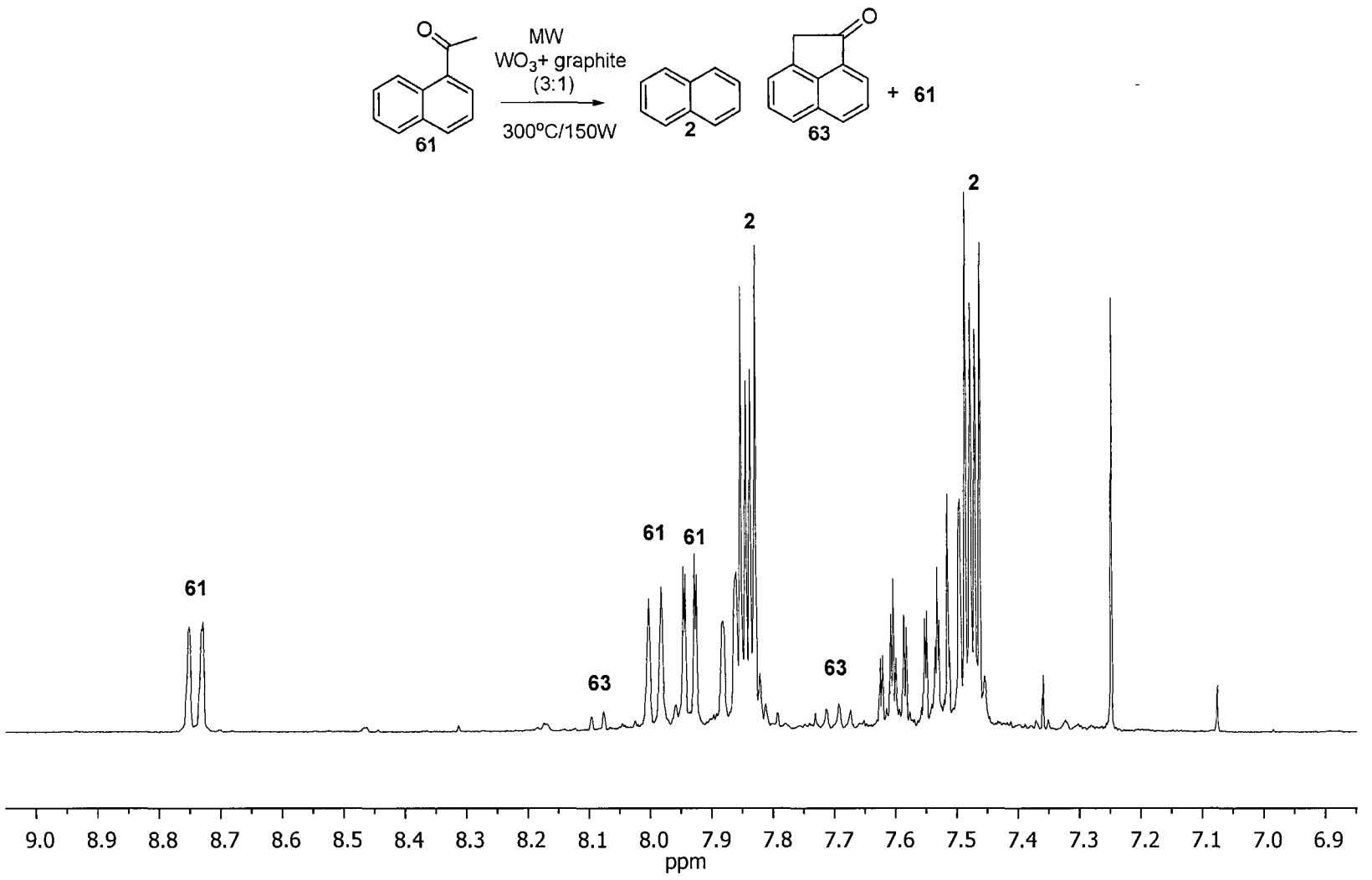

CH3
MW/graphite
300°C/150W
1 min
51
49
50
2
33
Pentane Extract

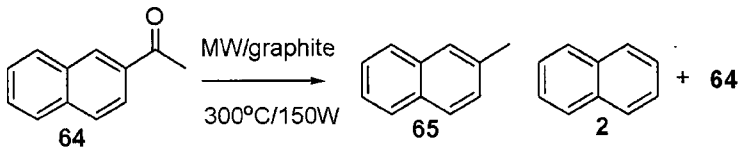

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

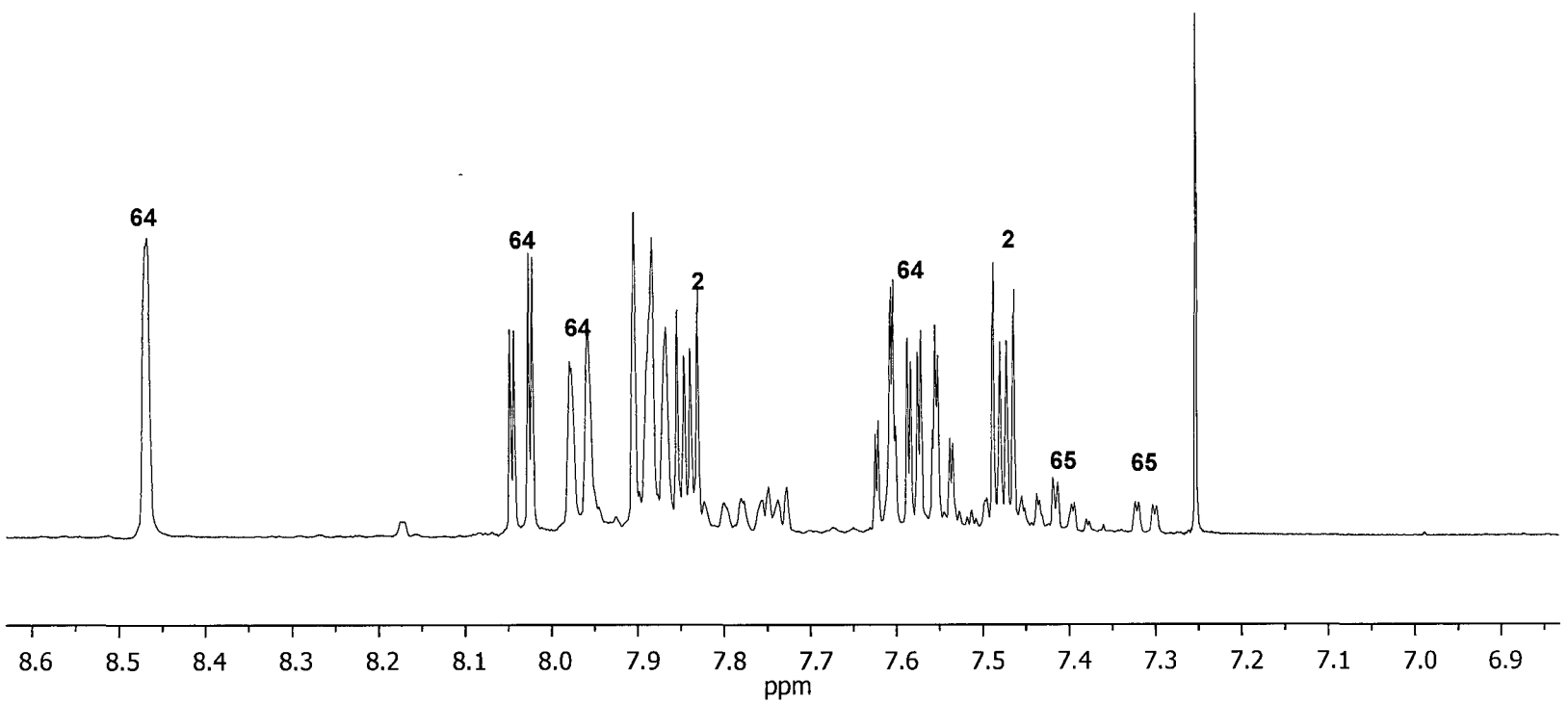

FVP
880°C/0.03 torr
61
2
66
65
+ 61
61
61
61
2
2
65
66
66
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
ppm


MW/graphite
300°C/150W
61
2
63
+ 61


61
63
61
61
2
63
61
61
2
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
ppm


MW
WO3+ graphite
(3:1)
300°C/150W
61
2
63
+ 61
61
63
61
61
2
63
2
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm


MW/graphite
300°C/150W
64
65
2
+ 64


64
64
64
2
64
2
65
65
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
ppm